Crystal symmetry and domain structure of morphotropic $Pb(Zr_{1-x}Ti_x)O_3$-ceramics

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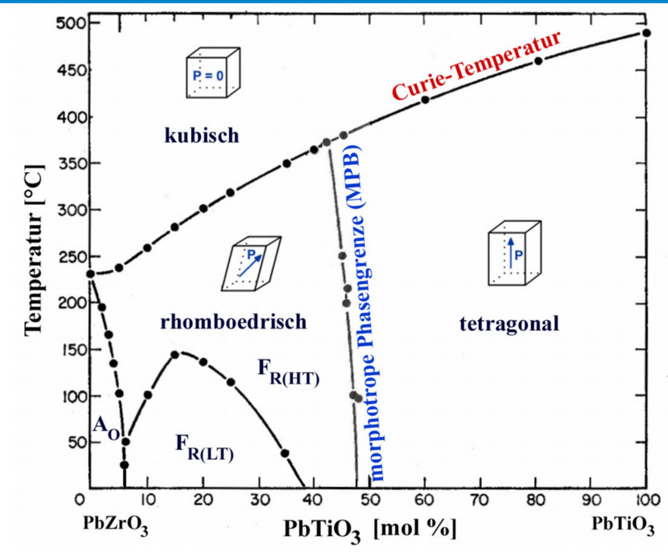
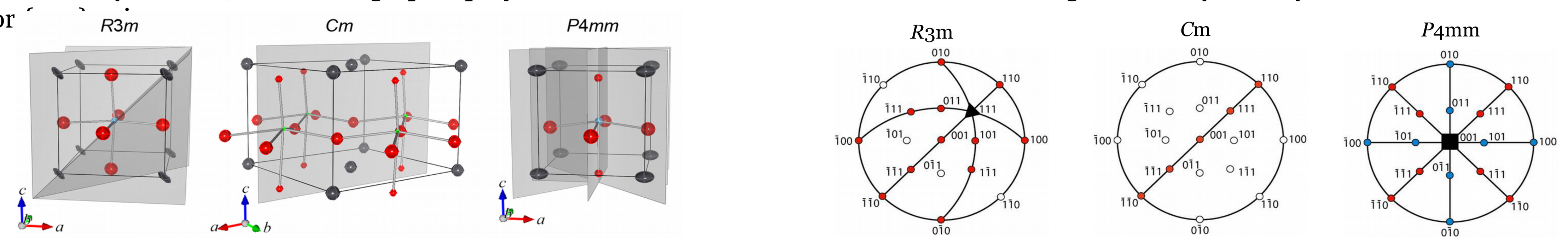
Abstract

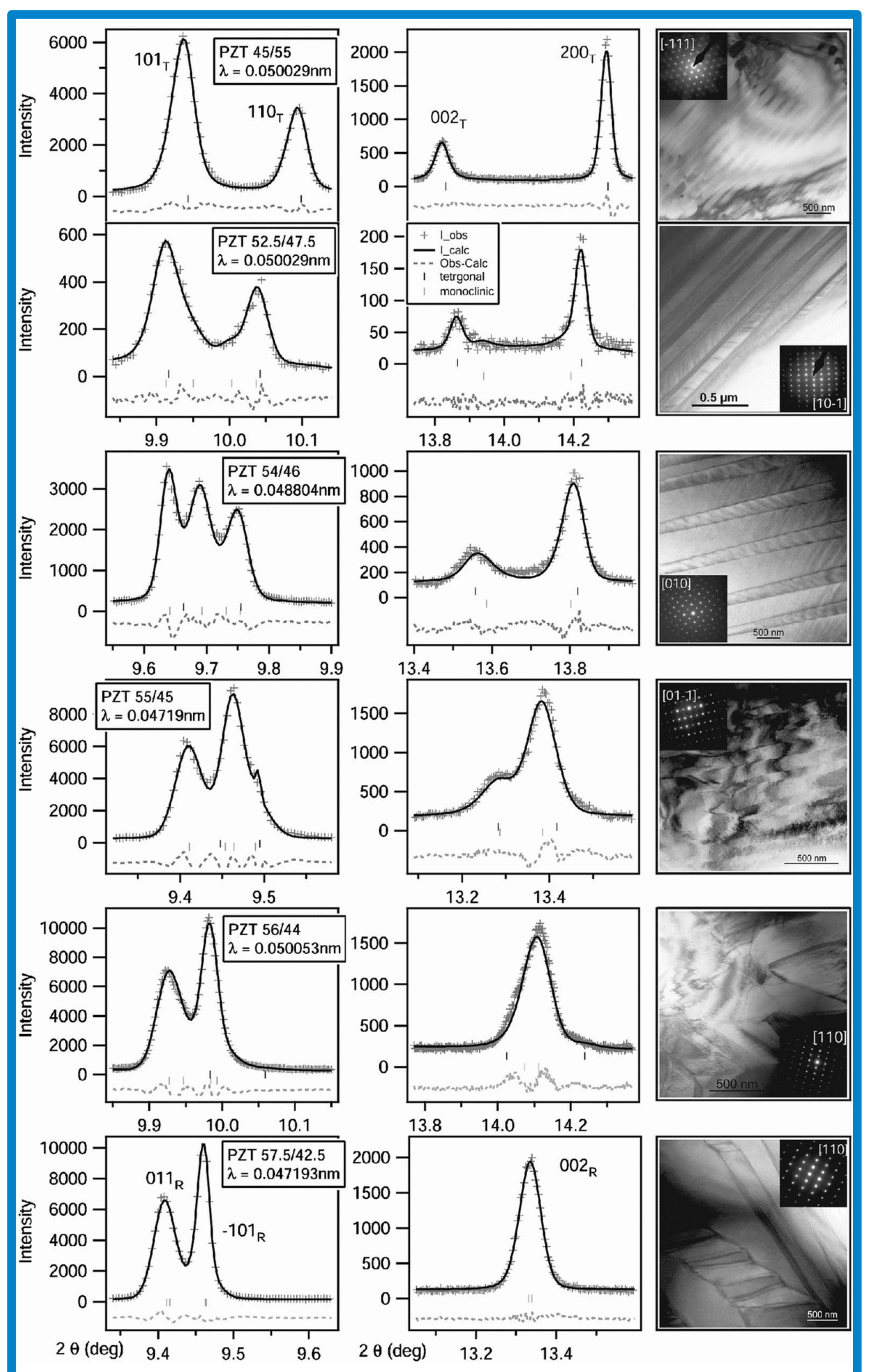
For technical applications based on the piezo- and ferroelectric effect the most common material used is PZT (PbZr1-xTixO3). While the processing and tuning of the material for different applications is mastered, there is still ambiguity in the understanding of the origin of the strong piezoelectric effect in this material. So far the coexistence of tetragonal and rhombohedral structure in proximity of the morphotropic phase boundary (MPB) [1] and the possible field induced phase transition was supposed to be responsible for the excellent properties. About ten years ago [2], based on high resolution x-ray powder diffraction data, a monoclinic structure was proposed for the MPB enabling new ways of explanations. But the existence of this monoclinic phase is still under debate [3], due to nanodomains that have been observed in morphotropic PZT via transmission electron microscopy [4]. The adaptive theory [5] can explain the additional reflections in x-ray diffraction, attributed to a monoclinic splitting, as superlattice reflections of stacked rhombohedral nanodomains. In this work the symmetry of the crystal structure is investigated within single domains by convergent-beam electron diffraction. Samples with compositions (1-x)/x ranging from 0/40 to 45/55 have been examined. The compositions up 60/40 up to 55/45 showed rhombohedral symmetry. For PZT 54/46 tetragonal as well as monoclinic symmetry were observed. With increasing Ti-content the monoclinic phase diminishes. For neighboring mooclinic domains in PZT 54/46 the determined orientations lead to a twin operation which is expected for a Cm as a subgroup of P4mm. The inverse transition from monoclinic to tetragonal symmetry was observed for the same composition in an in situ heating experiment accompanied by vanishing of those nanodomains. Therefore the nanodomains are attributed to the monoclinic phase. Nethertheless coexistence of different phases is observed.



Crystal structures:

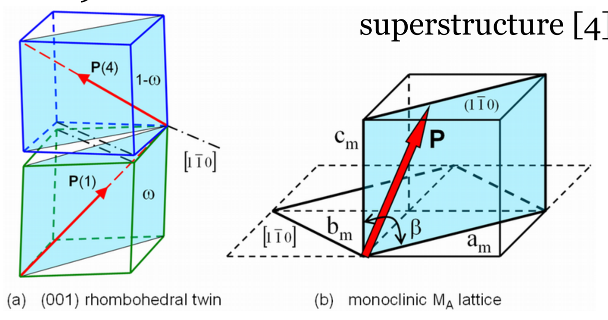
To the left the phase diagram by Jaffe et al. [1]Is shown. In the middle the crystal structures R3m (rhombohedral), Cm (monoclkinic) (Cm) and P4mm (tetragonal) as determined by XRD [2] are displayed [6] with their mirror planes shown in transparent grey. For explanation of the crystal symmetry determination by CBED [7] the stereographic projections are shown with the zone axes containing a mirror symmetry are marked in red for {110} -mirror and blue for



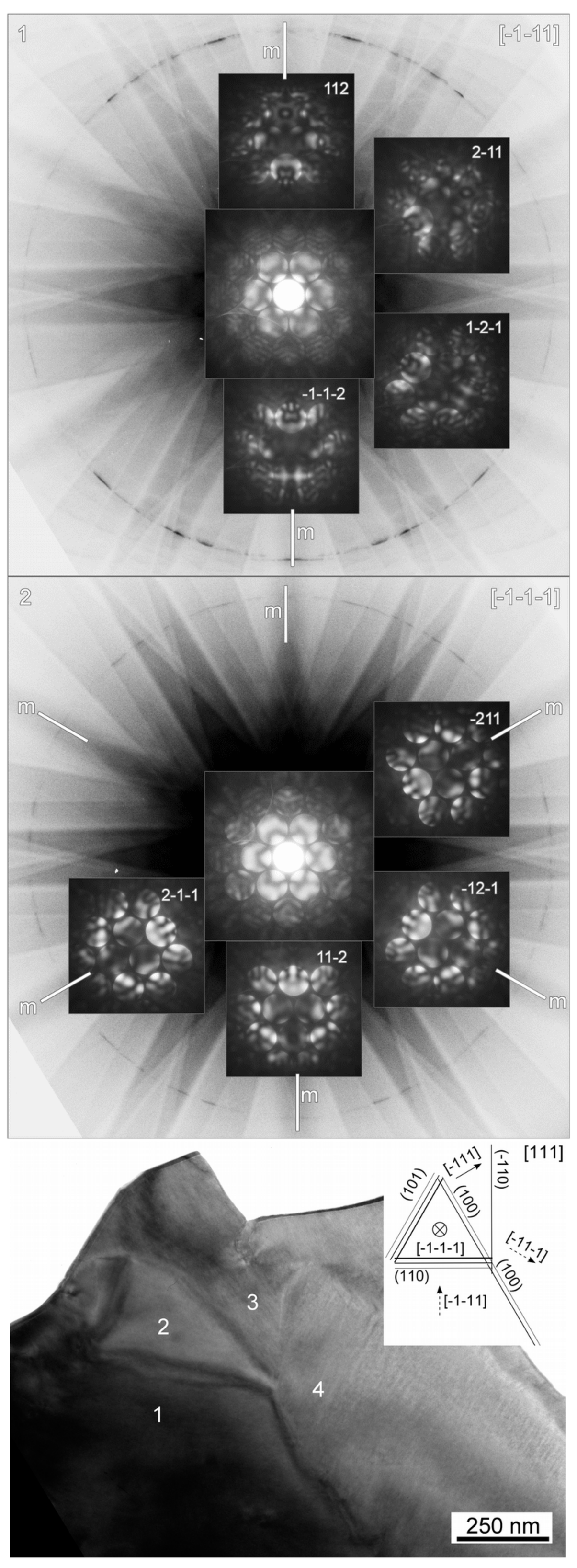


XRD: Diffraction patterns [2] of morphotropic PZT composition show extra reflections which can be attributed to monoclinic [3] structure or Interpreted as adaptive reflections [4] caused by nanodomains, which are observed in the TEM [5].

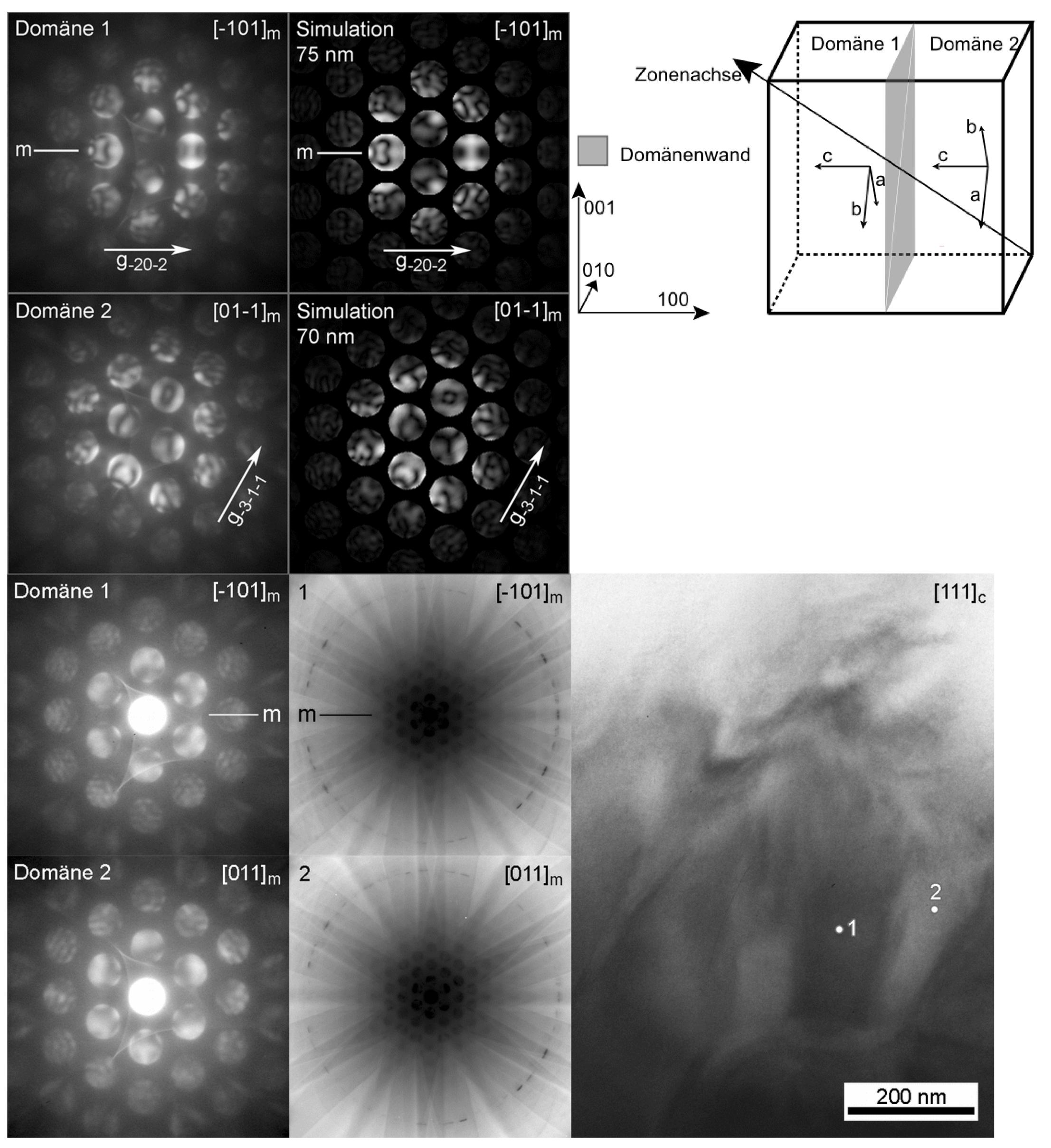
Adaptive theory: Model of rhombohedral 109° nanodomains that mimic monoclinic superstructure [4].



Convergent-Beam Electron Diffraction

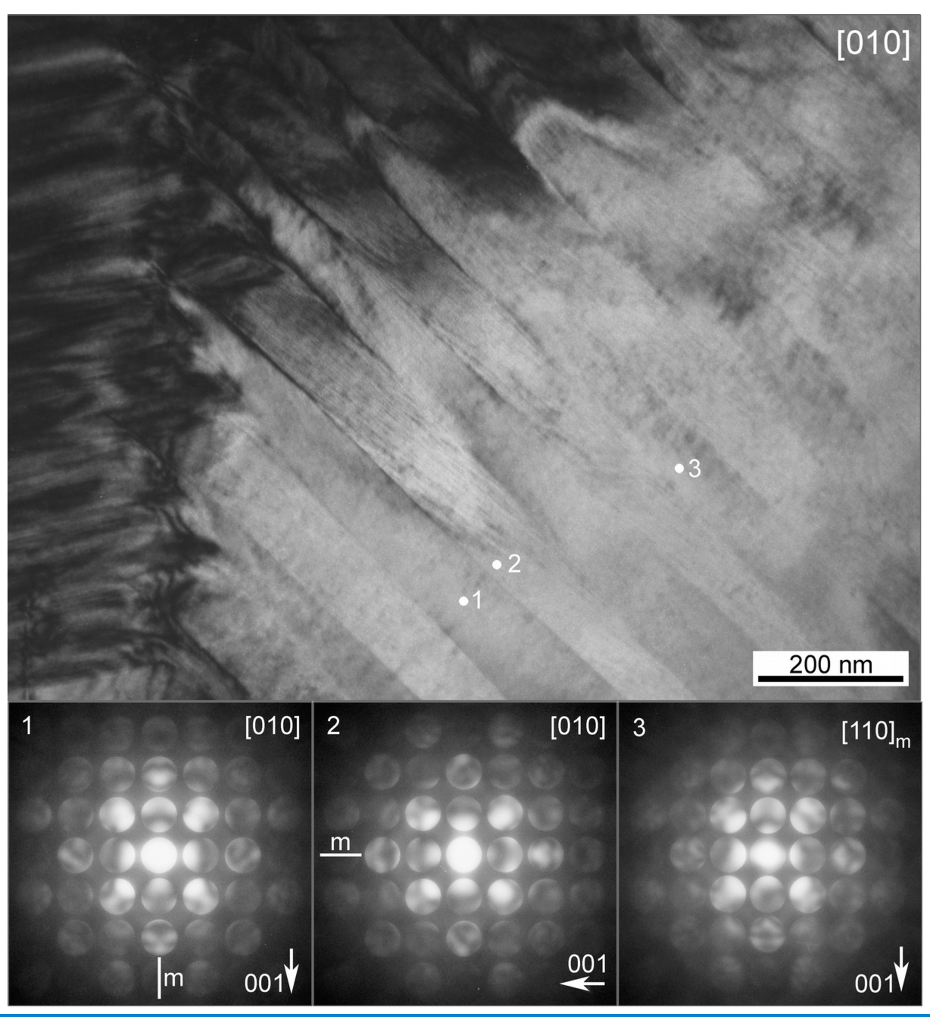


PZT 55/45: Rhombohedral Domain configuration CBED-patterns of domain 1 and 2 from which rhombohedral symmetry and orientation can be retrieved [7].

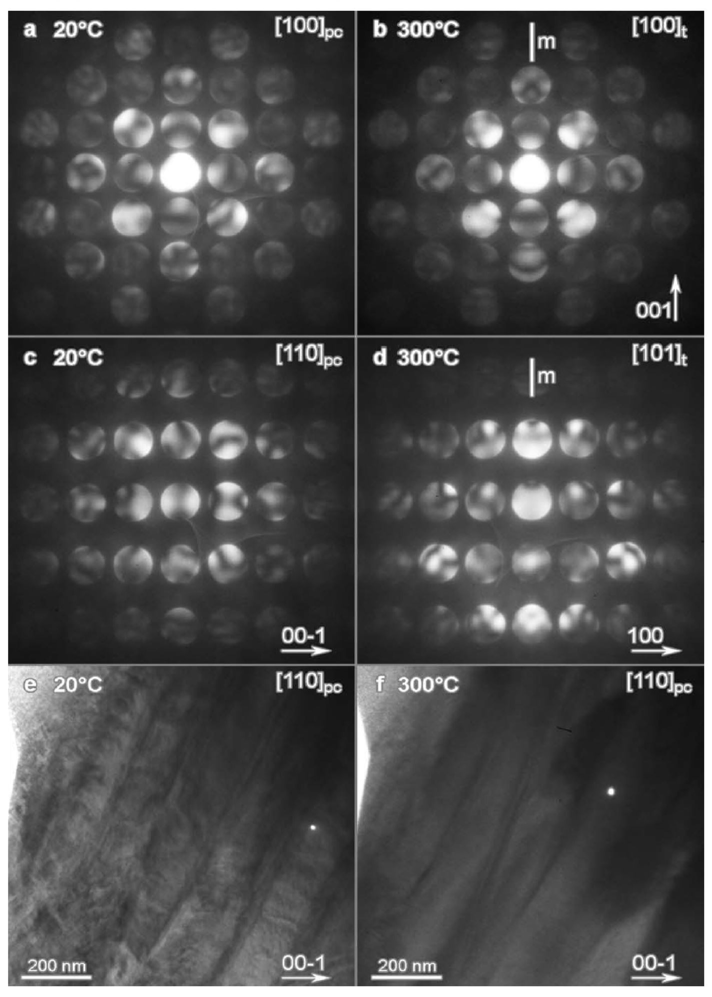


PZT 54/46: <111>pc CBED- patterns [8] of neighboring monoclinic domains revealing their twin relationship of 90° roation about c* after comparison with simulations [9] in agreement with *Cm* as a subgroup of P4mm [10].

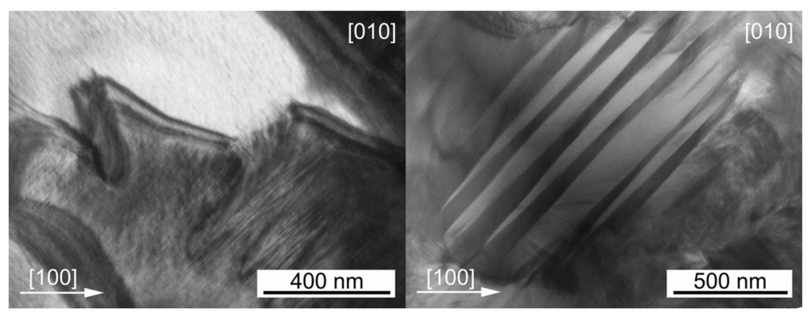
PZT 54/46: Tetragonal 90°-domains were found (1 and 2) but also domains without symmetry (3) according to monoclinic structure [4].



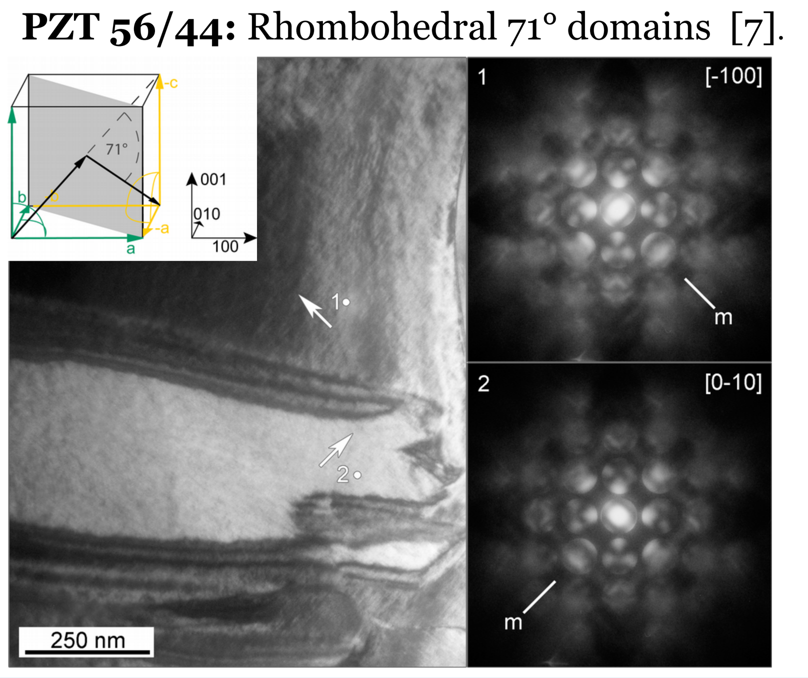
PZT 54/46 *in situ* heatiing experiment: With temperature at 300°C nanodomains present at RTR disappear and tetragonal mirror plane appears in CBED-patterns.



PZT 54.5/45.5: Rhombohedrallike (left) and tetragonallike Domain configuration coexist in this composition at RT [5].

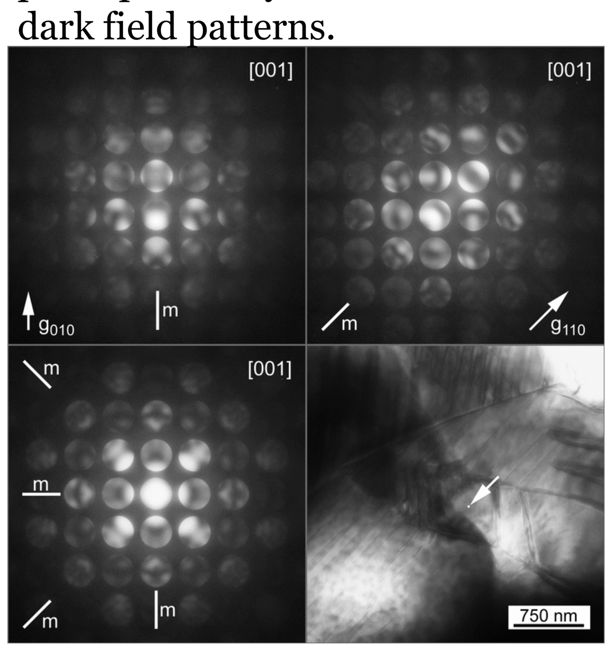


PZT 56/44: Rhombohedral 71° domains [7].



PZT 45/55:

Fourfold symmetry in a c-domain and the (-110)- and (100) mirror plane proved by zone axis and dark field patterns.



Bibliography

[1] W. R. Jaffe *Piezoelectric Ceramics*, Academic Press New York (1971)
[2] B. Noheda *Rev. B* **63**(1): 014103 (2001)
[3] K.A. Schönau *et al. Phys. Rev. B* **75** 184117 (2007)
[4] L.A. Schmitt et al. J. Appl. Phys., **101**, 074107 (2007)
[5] Y. U.Wang *Phys. Rev. B* **76** (2): 024108 (2007)
[6] Momma and Izumi *J. Appl. Cryst.* **41** (2008) 653
[7] R. Schierholz et al. *Phys. Rev. B* **84**, 064122 (2011)
[8] R. Schierholz et al. *Phys. Rev. B* **78**, 024118 (2008)
[9] K. Tsuda *et al. Acta* **A55** (1999) 939
[10] R. Schierholz et al. *J. Appl. Cryst.* **45** (2012) 766

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