# Influence of Grain Size on Temperature Dependence of Electric Field Induced Strain in Morphotropic PZT Ceramics

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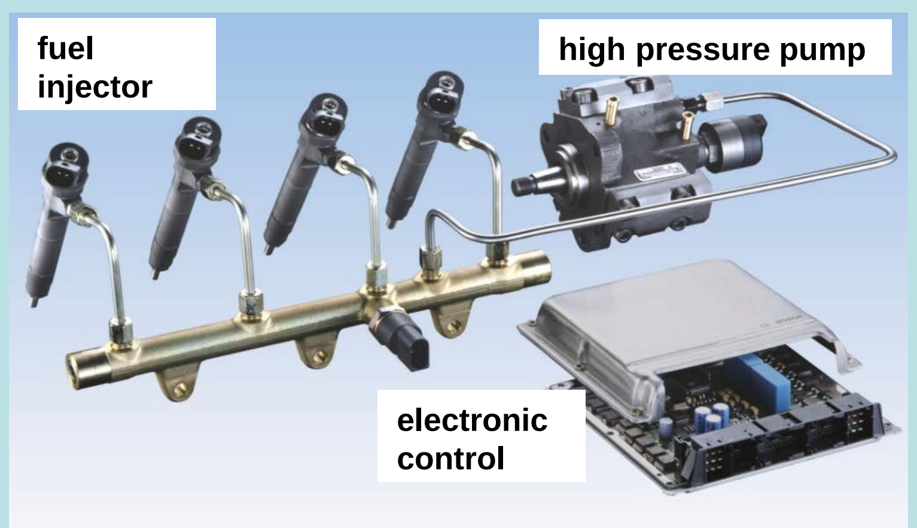
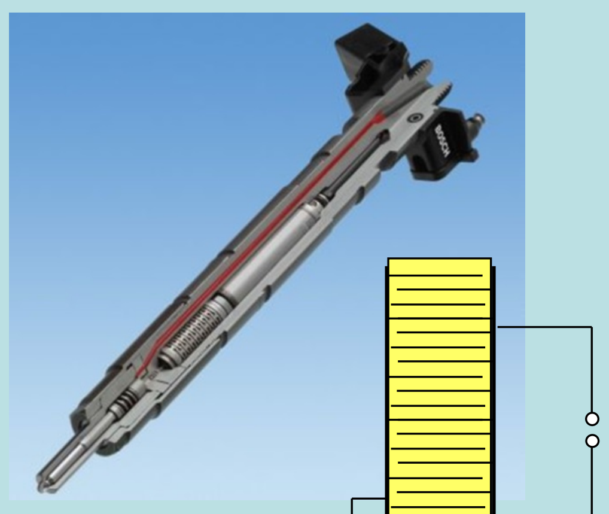
## Applications of piezoelectric actuators in automobiles

Fuel injection system

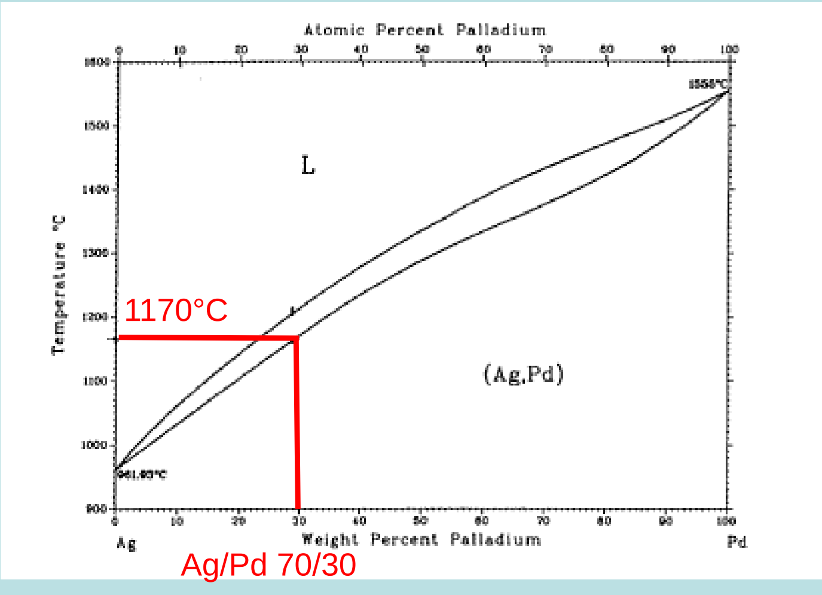


Piezoactuator driven fuel injector



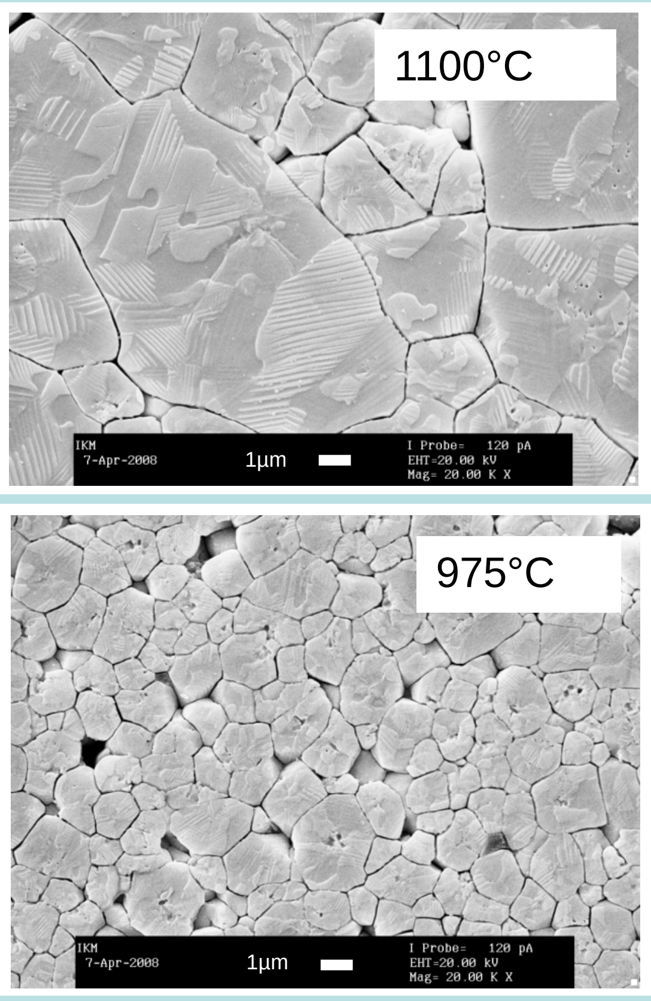
Source: Bosch

Ag-Pd phase diagram

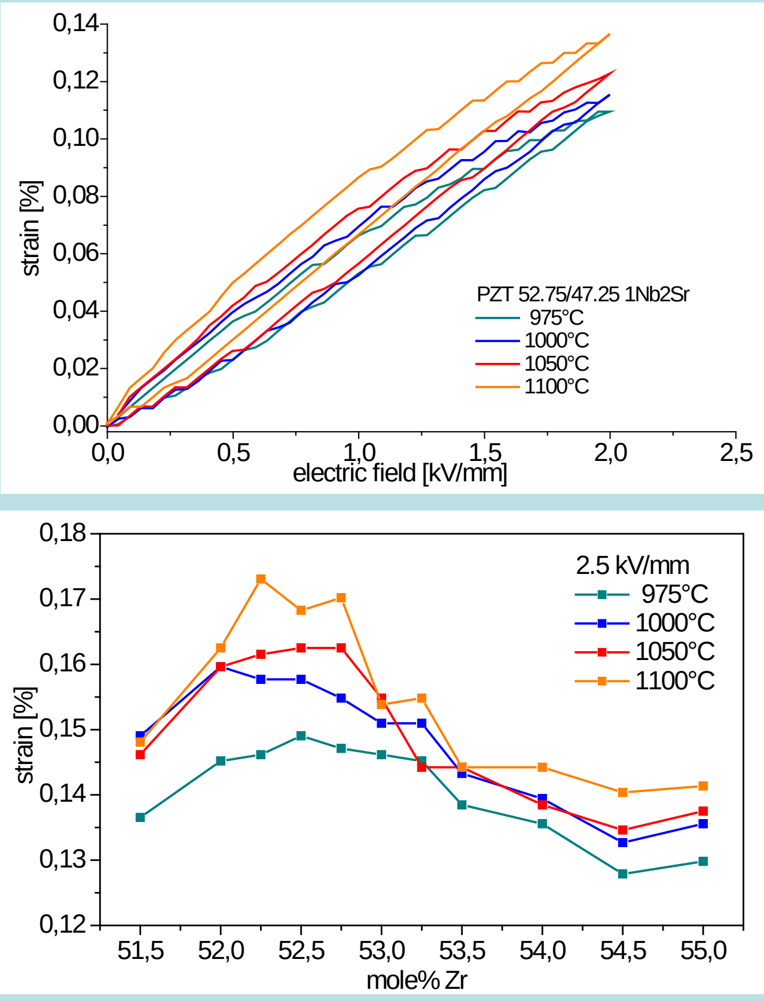


For a decade high performance fuel injection systems in automobiles are operated by piezoelectric multilayer actuators. The electric field induced strain of soft-doped PZT is used to control the injection valves in these devices, designed for operating temperatures from -40°C to 160°C. Field induced strain and its temperature behaviour are very important parameters characterizing the performance of the ferroelectric materials. With respect to processing of the devices, a major challenge is the reduction of sintering temperature when cofiring the PZT multilayer actuators, in order to avoid high Pd contents in the Ag-Pd alloys used for inner electrodes. As a consequence of lower sintering temperature, grain size becomes smaller. Therefore, the effects of reduced grain size on strain and strain-temperature characteristics are of high technological interest.

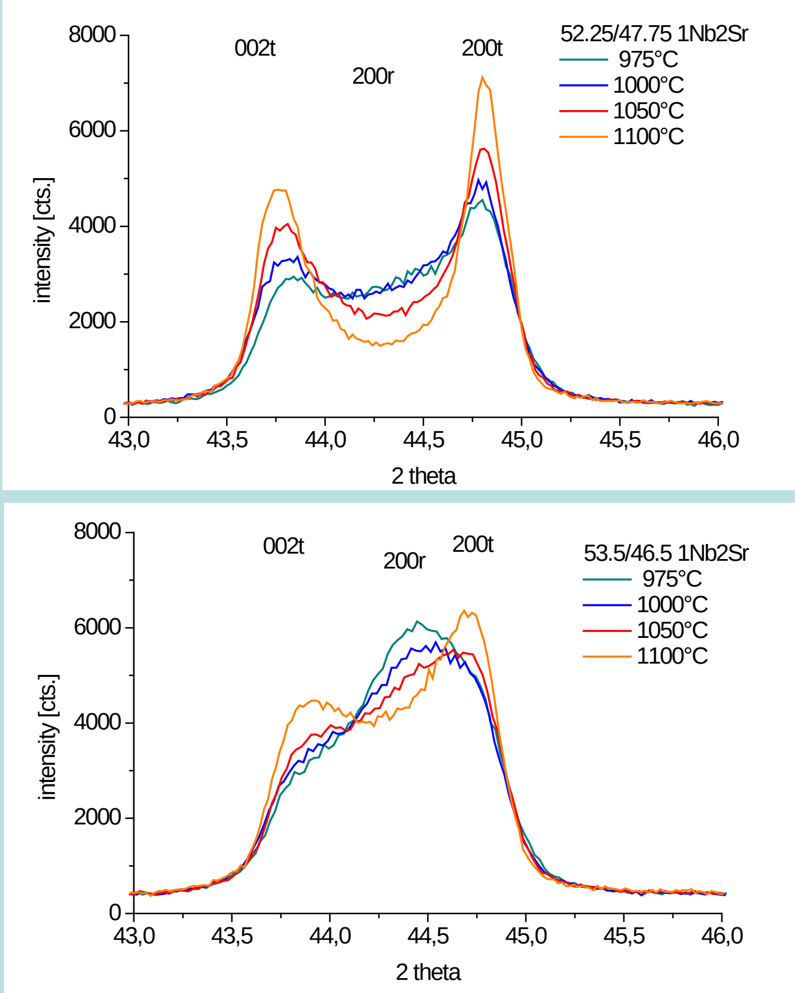
## Grain size effects on strain at ambient temperature



Microstructure of PZT1Nb2Sr sintered at 975°C and 1100°C



Electric field induced strain in PZT 1Nb2Sr sintered at temperatures from 975°C to 1100°C

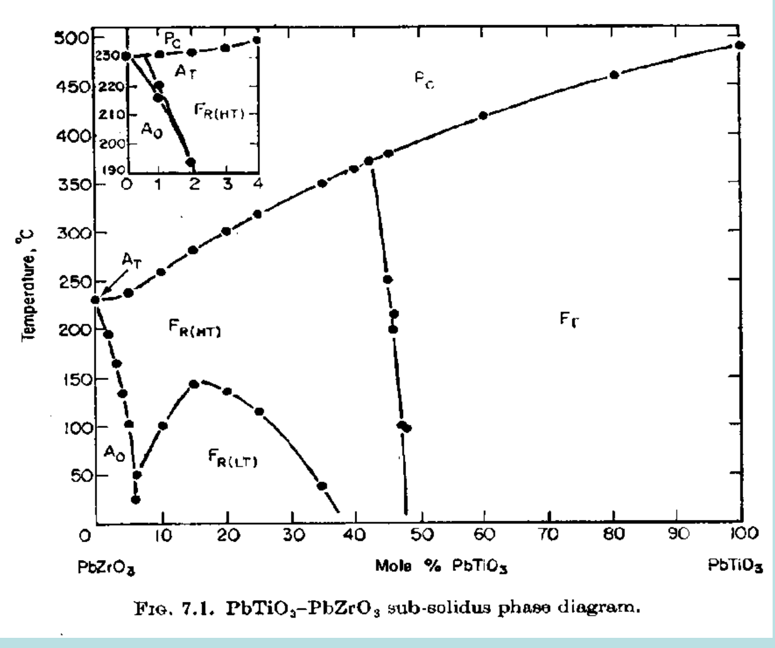


X-ray diffraction patterns (200 reflections) of PZT1Nb2Sr sintered at 975°C to 1100°C

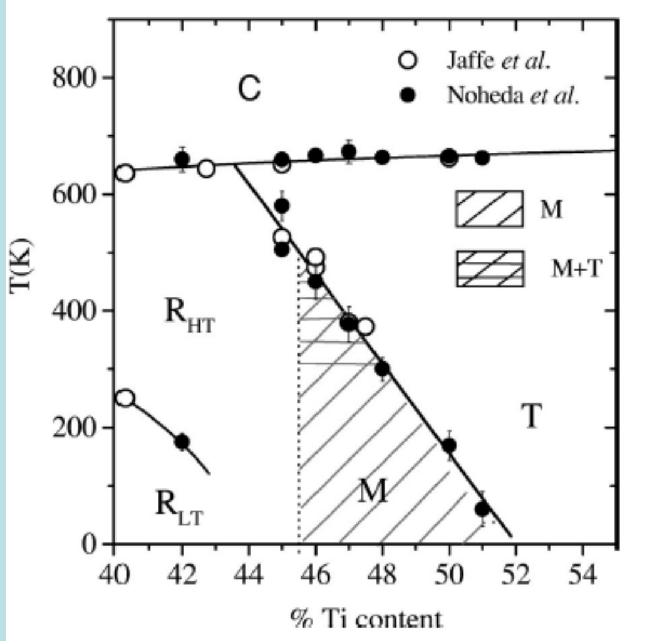
When lowering the sintering temperatures from 1100°C to 975°C the grain size is reduced from 3µm to 1 µm and the field induced strain decreases. Quantitatively the decrease in grain size is similar, whereas the reduction in strain is different depending on composition. The differences in the effects of grain size on field induced strain are attributed to changes in phase composition (Kungl and Hoffmann (2010)).

## Structure of PZT at the morphotropic phase boundary

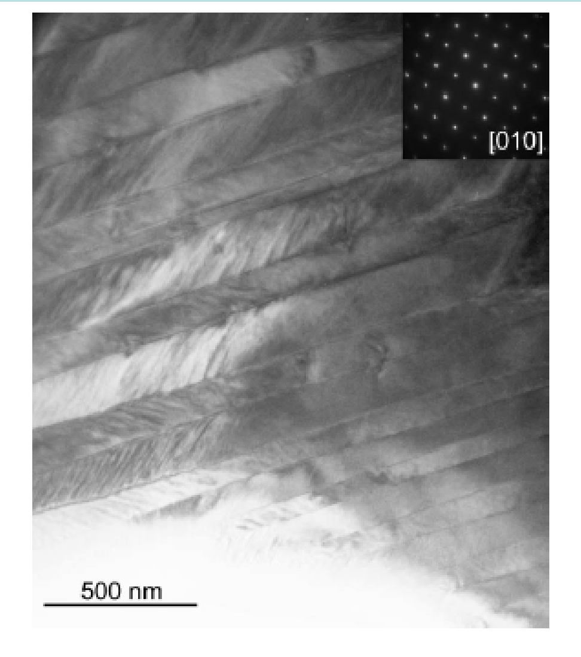
PZT phase diagram (Jaffee 1974)



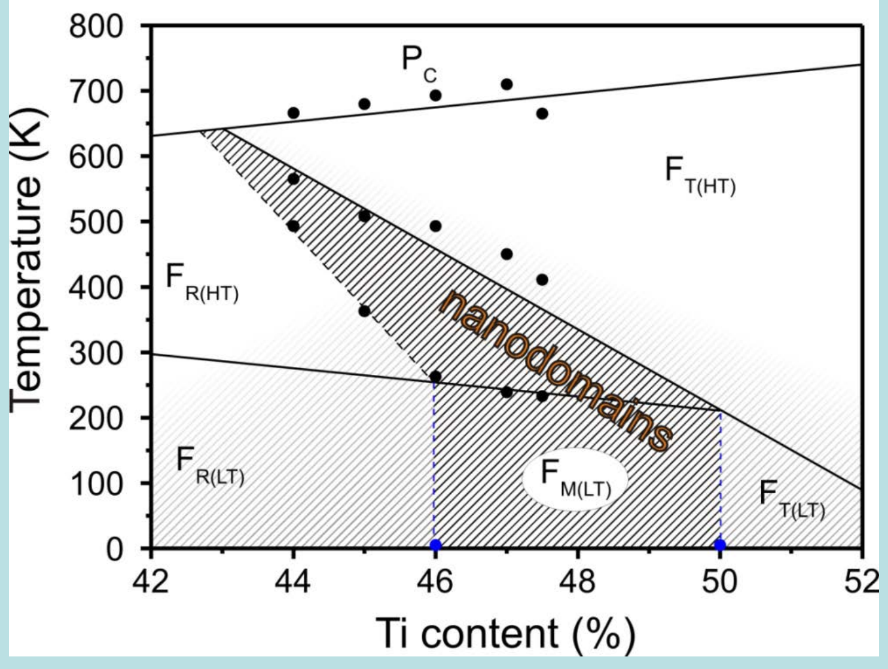
PZT phase diagram (Noheda 1999)



Nanodomains in PZT 52.5/47.5 Schmitt et al (2007)



Phase diagram for La-doped PZT with existence region of nanodomains (Hinterstein et al. (2010)

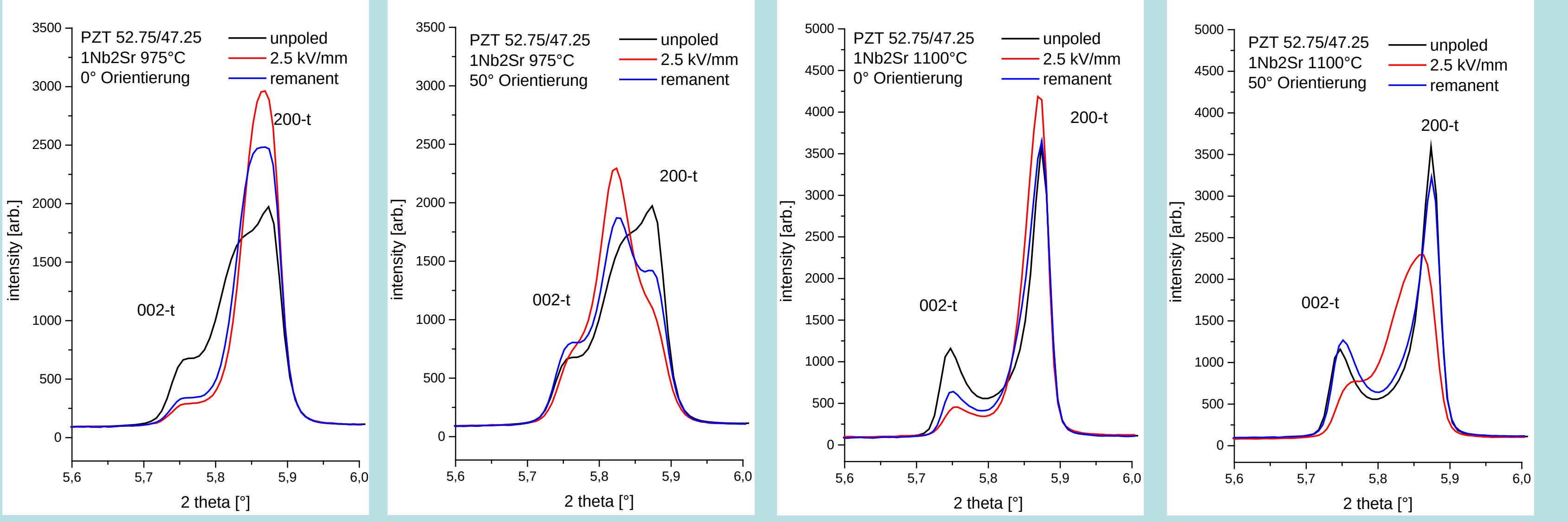


According to the conventional description of the structure of PZT at the morphotropic phase boundary there is a two phase coexistence region of tetragonal P4mm and rhombohedral R3m (Jaffee 1971). In 1999 Noheda et al. suggested the presence of a monoclinic phase in PZT with compositions containing 52 to 55 mol% $ZrO_2$.

Subsequent investigations of the microstructure by Schmitt et al. (2007) identified the formation of nanodomain structures in this compositional range. Schoenau et al. (2007) correlated the diffraction intensity not attributable to tetragonal or rhombohedral phase to the effects of non-Bragg type diffraction resulting from the nanodomain structure. The coherently scattering tetragonal nanometer-sized domains give rise to x-ray patterns, which can be indexed as monoclinic.

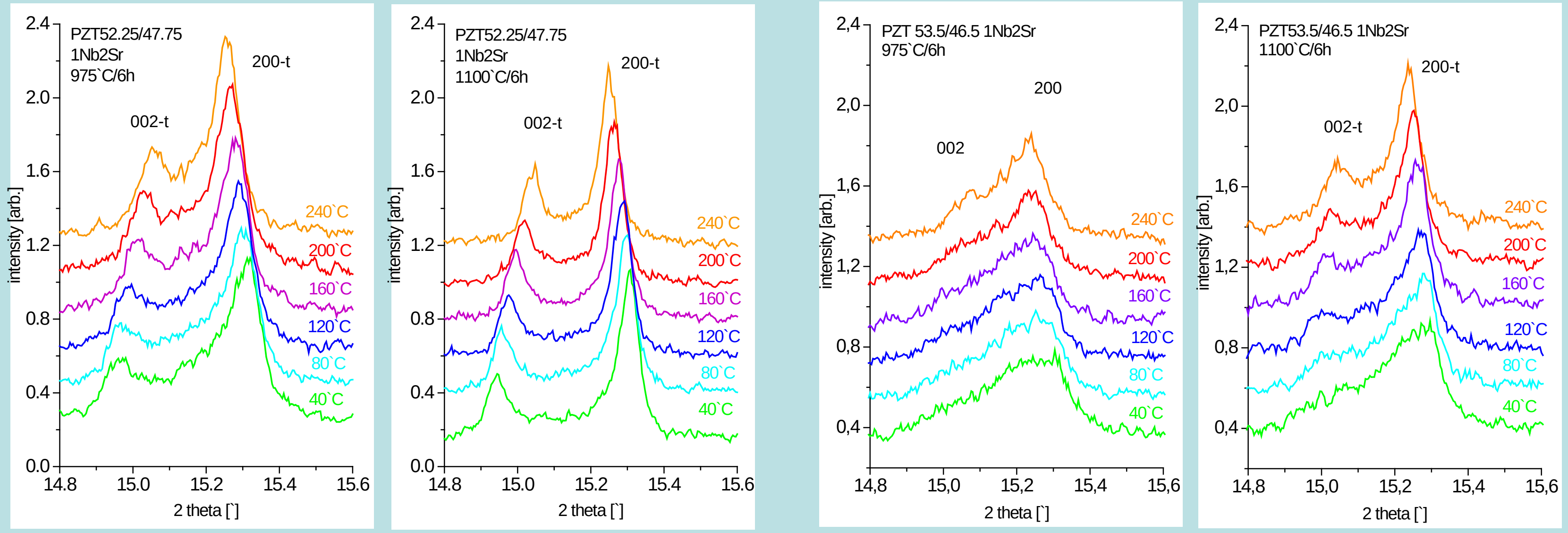
*In-situ* transmission electron microscopy investigations with applied electric field on undoped PZT 54/46 by Theissmann et al. (2007) indicated, that mainly the nanodomains respond to the electric field while the microdomain structure did not change noticeably in these experiments. Based on neutron diffraction and synchrotron X-ray measurements a phase diagram indicating the existence region of the nanodomains was established by Hinterstein et al. (2010). Nanoscale regions with monoclinic structure coexisting with tetragonal or rhombohedral PZT were observed using CBED by Schierholz and Fuess (2011).

## *In-situ* x-ray diffraction electric field for PZT with different grain size



Electric fields applied to PZT with the same composition but different grain size lead to activation of different strain mechanisms. In the large grained PZT 52.75/47.25 1Nb2Sr ($T_{sint}$ = 1100°C) ceramics domain switching is the most pronounced strain mechanism, as indicated in the change of intensities of the tetragonal 200 and 002 reflections. In contrast to that in the fine grained ($T_{sint}$ = 975°C) material marked effects from a phase transformation were identified.

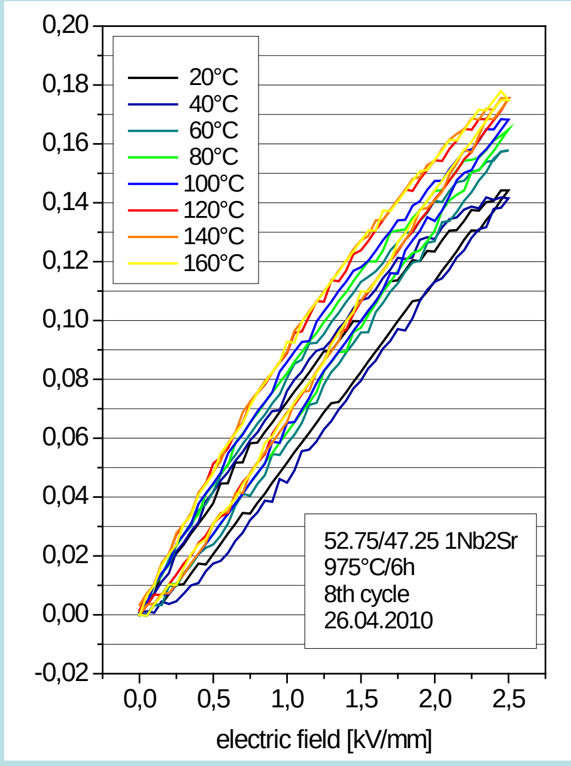
## Temperature dependence of structure for PZT ceramics with different grain size



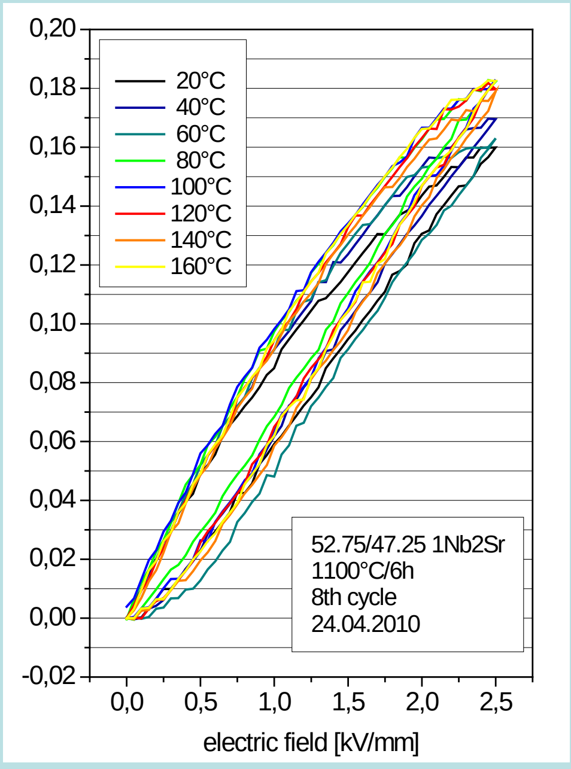
With temperature increase most marked structural changes in PZT from the tetragonal side of MPB (PZT 52.25/47.75 1Nb2Sr) are reduction of the lattice distortion c/a. Coarse grained ceramics with compositions from the rhombohedral side close to MPB (PZT 53.5/46.5 1Nb2Sr) undergo a temperature induced phase transition. In contrast to the coarse grained PZT, no transition to tetragonal structure was found for fine grained materials of the same composition up to 240°C.

## Temperature dependence of strain for PZT 1Nb2Sr ceramics with different grain size

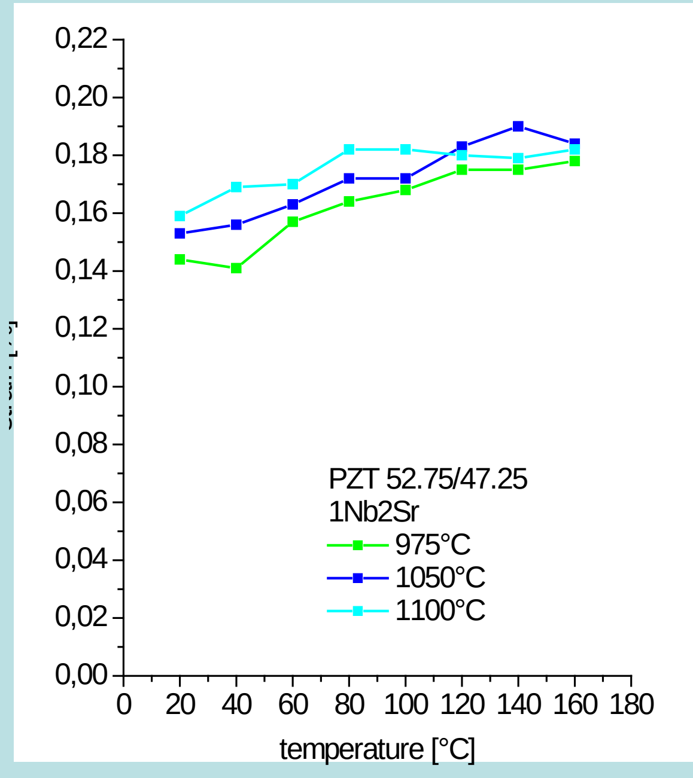
975°C



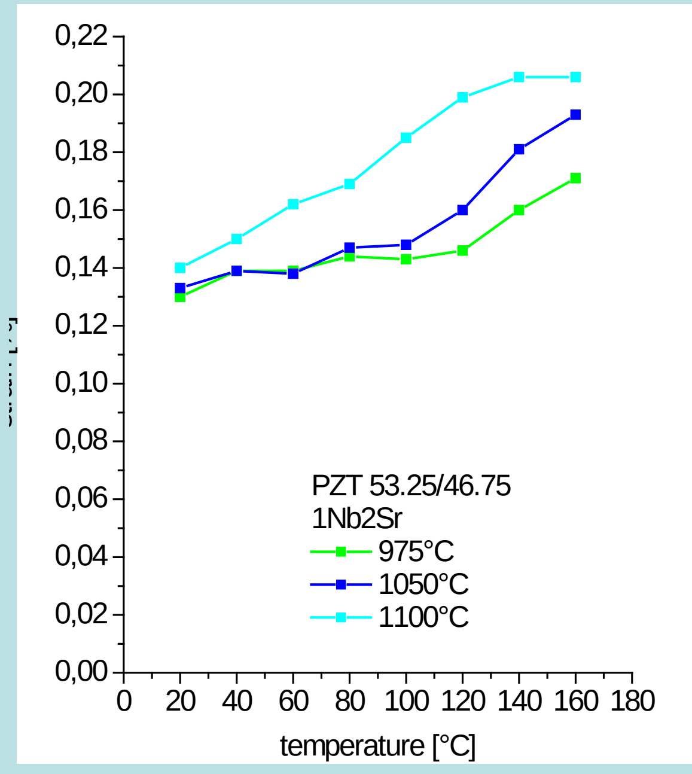
1100°C



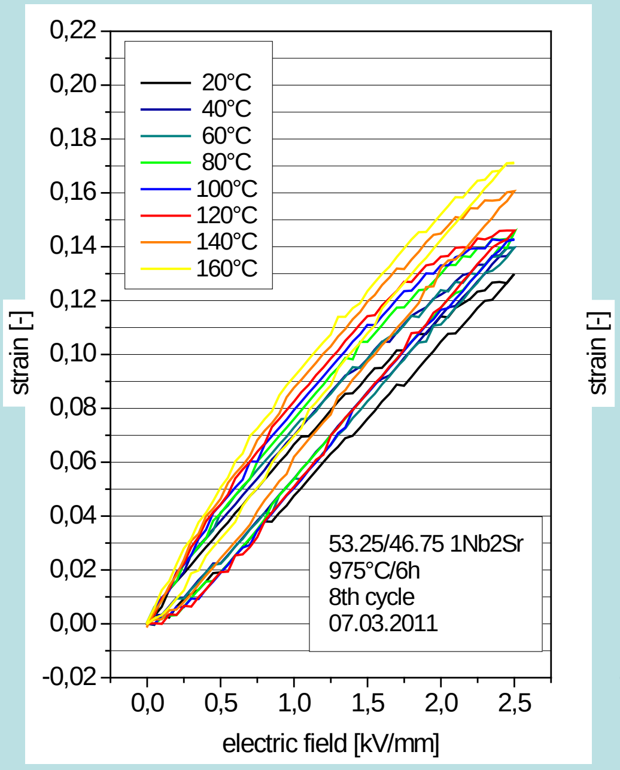
PZT 52.75/47.25 1Nb2Sr



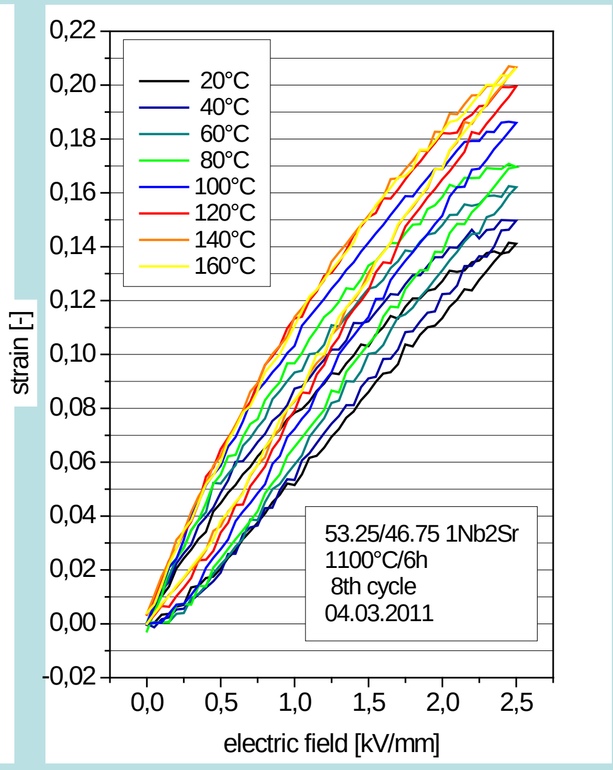
PZT 53.25/46.75 1Nb2Sr



975°C



1100°C



In PZT from the tetragonal side of the phase boundary (PZT 52.75/47.25 1Nb2Sr) both, coarse and fine grained materials show a similar increase in strain with temperature. The strain is slightly lower for the fine grained ceramics. The strain vs. temperature characteristics are approximately linear. The moderate decrease in lattice distortion at higher temperatures leads to enhanced domain switching and higher field induced strain .

In coarse grained PZT with compositions from the rhombohedral side close to MPB (PZT 53.25/46.75 1Nb2Sr) a pronounced nonlinear increase in strain with temperature was found. The material undergoes a temperature induced phase transition (Kungl and Hoffmann 2007). In contrast to that, fine grained materials of the same composition did not show marked nonlinearity of strain within the temperature range under investigation. The temperature induced phase transition in the fine grained materials seems to be shifted to higher temperatures.

## Summary and Acknowledgements:

Coexistence of phases and formation of nanostructures are the characteristic structural and microstructural features of morphotropic PZT ceramics. Monoclinic structures are limited to small regions coexisting with tetragonal and/or rhombohedral volume fractions. Coherent scattering from nanometer-sized domains results in x-ray patterns, which can be indexed as monoclinic. Analysis of structure by diffraction techniques has to take the effects from real structure into account.

In morphotropic PZT ceramics smaller grain size reduces the field induced strain. Along with variations in grain size there are changes in structure which modify the strain mechanisms and lead to quantitatively different strain-grain size dependence for different compositions. With increasing temperature the c/a ratio of tetragonal phase diminishes; with high tetragonal volume fraction the strain temperature characteristics are approximately linear. Coarse grained PZT ceramics with substantial non-tetragonal volume fraction undergo a temperature induced phase transition, which leads to a strong increase in strain and a non-linear strain-temperature behavior. For fine grained PZT the onset of phase transition is shifted to higher temperature.

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