SFB 595

Deutsche Forschungsgemeinschaft

DFG

Grain Size Effects on the Electromechanical Properties of donor-doped PZT-Ceramics

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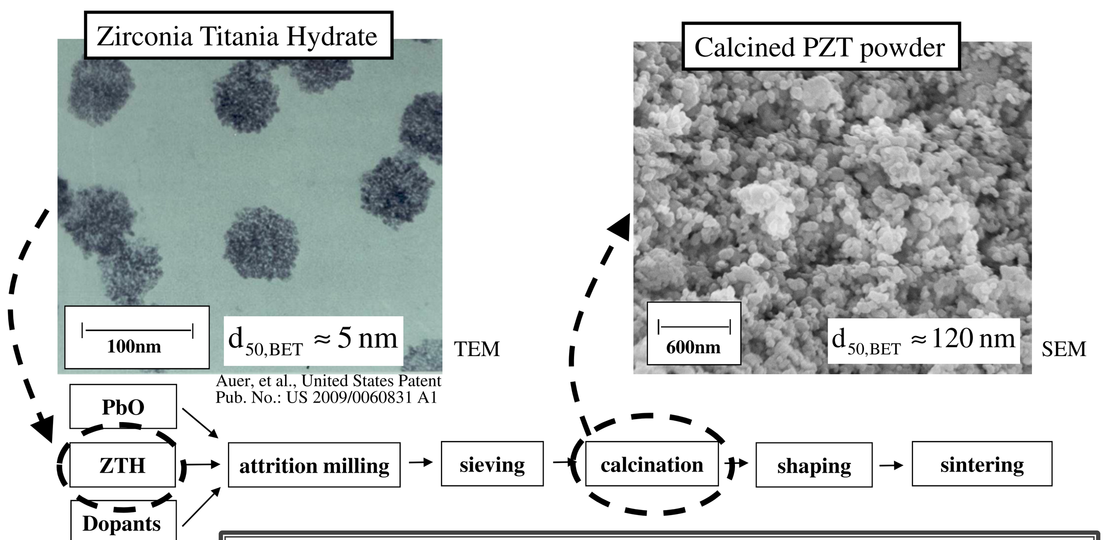
Motivation, Methods and Objectives

Piezoelectric ceramics of the solid solution $PbZr_{1-x}Ti_xO_3$ (PZT) are state of the art materials in sensor applications such as accelerometers and ultrasonic sensors. It is known from literature that their electromechanical properties are grain size dependent.

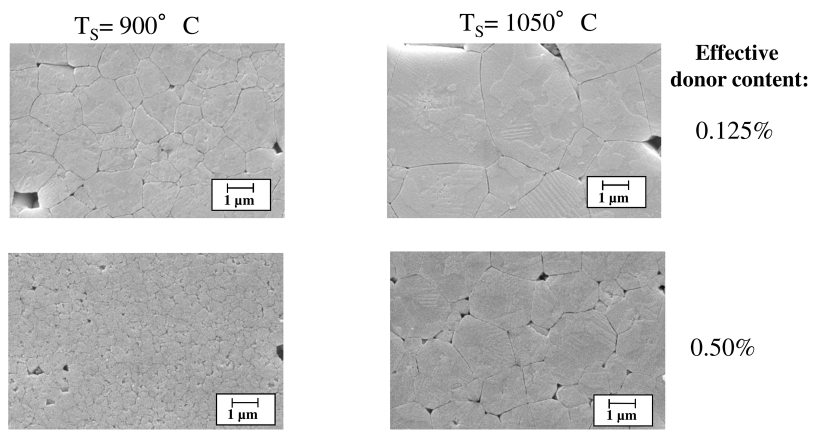
The current study analysed the grain size effect for different Zr/Ti-ratios and different donor concentrations. Dense ceramics with a grain size between 0.3 – 10.0 µm were obtained by varying the sintering temperature from 875°C to 1250°C. Hereby the Ti content was varied between 45 to 52 mol% with a fixed concentration of 1 mol% La as dopant. In a second step the Ti content was fixed at 47 mol% and the doping content was varied from 1 mol% La to co-doping with 1 mol% La and 0.75 mol% Fe.

While decreasing the grain size of the material a critical size was found, at which the domain structure changes significant from complex 3-D structures to simple lamellar patterns. This is in correlation with a suppression of the distortion of the perovskite lattice below the critical grain size as shown by XRD and Raman experiments. Small and large signal dielectric and piezoelectric properties show changes in non-180° domain switching as well as changes of the intrinsic piezoelectric properties by decreasing the grain size. It is demonstrated that the critical grain size is mostly related to the amount of donor dopant.

Synthesis and microstructure



Fine grained PZT powder by using conventional PbO and ZTH as raw materials



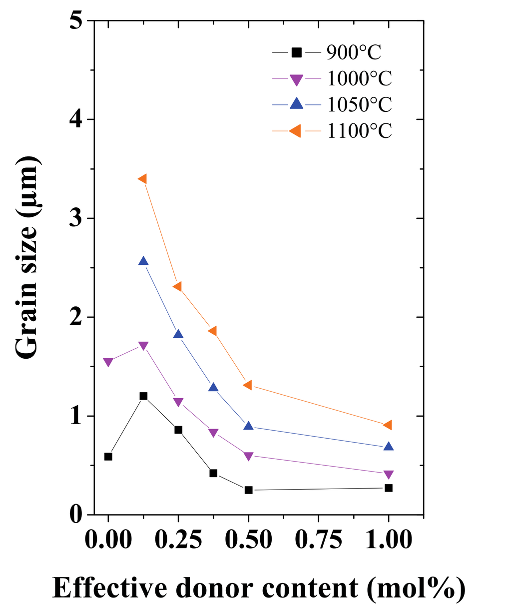
Doping of PZT ceramics :

$Fe\ (B\text{-site-aceptor}): 0.75Fe^{3+} = 0.375V_O^{\bullet\bullet}$

$La\ (A\text{-site-donor}): 1La^{3+} = 0.5V_{Pb}''$

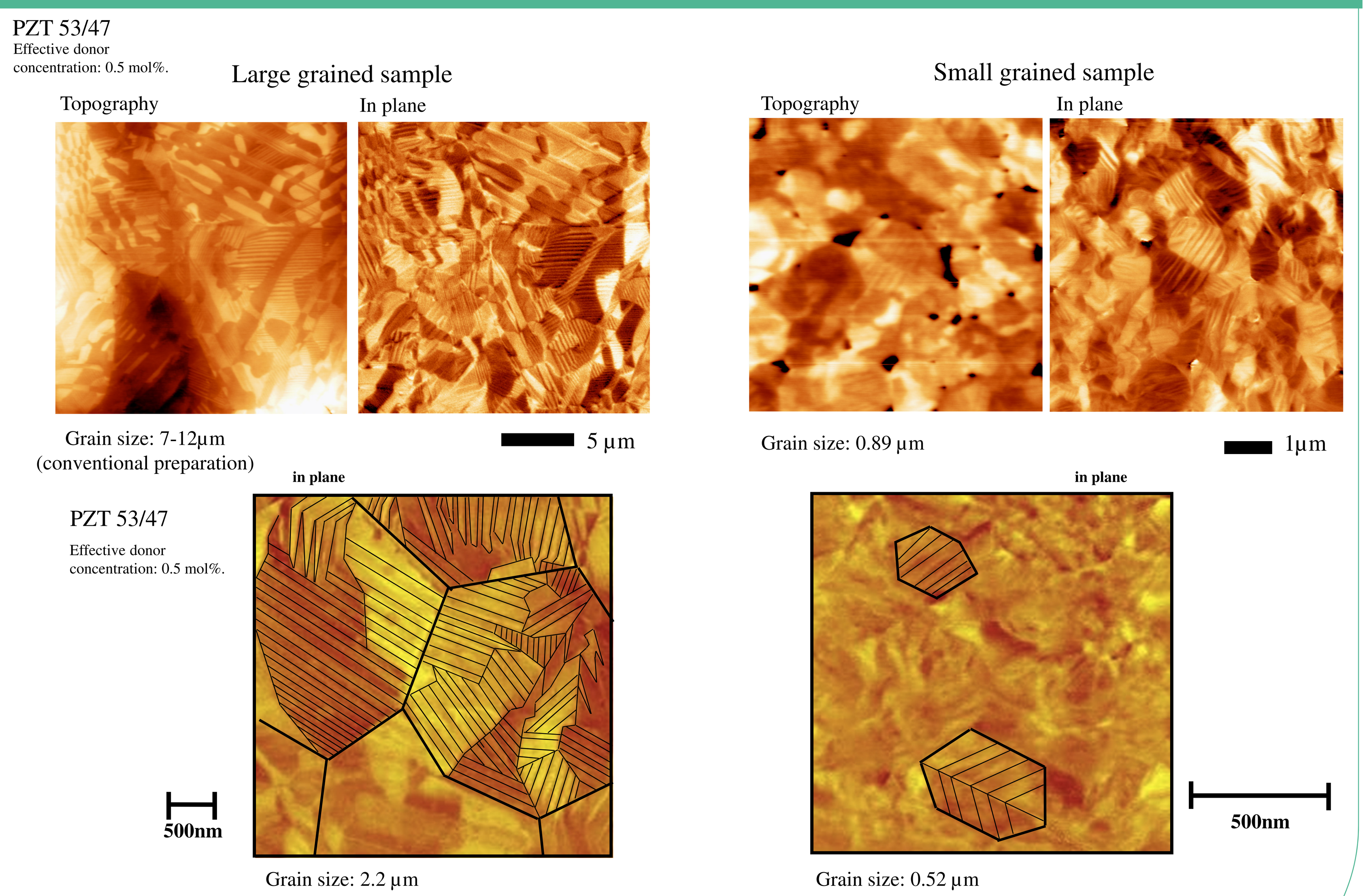
$\text{eff. donor content} = V_{Pb}'' - V_O^{\bullet\bullet} = 0.125\ \text{mol\%}$

Effective donor content



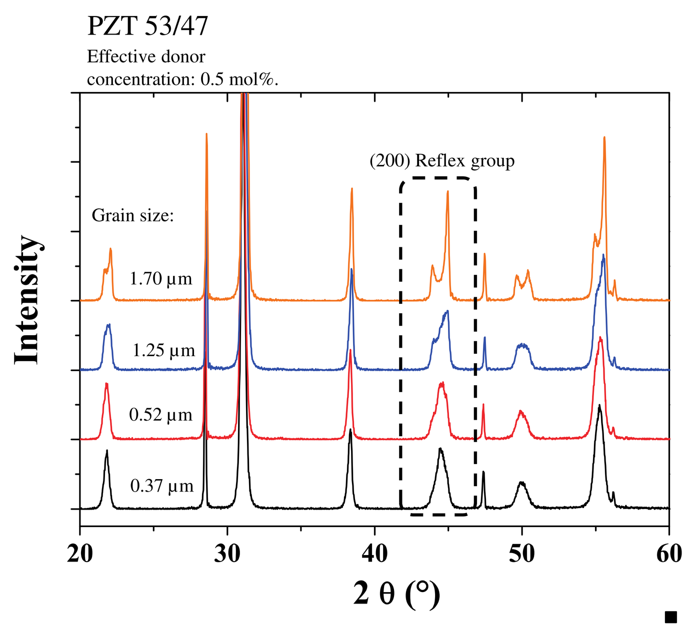
Control of the grain size by sintering parameters and effective donor content.

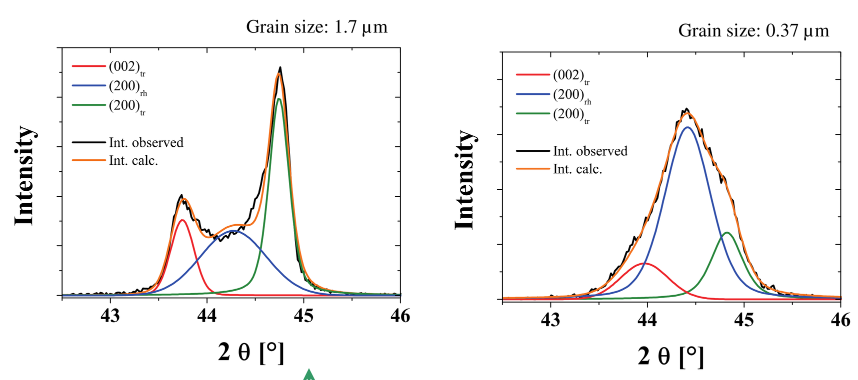
PFM analysis of the domain structure

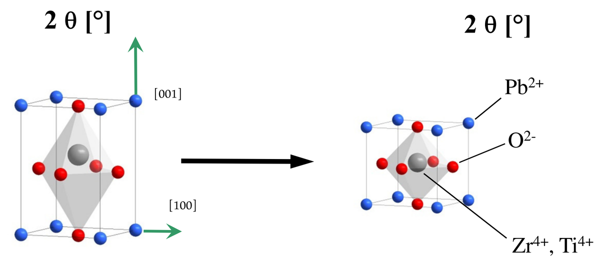


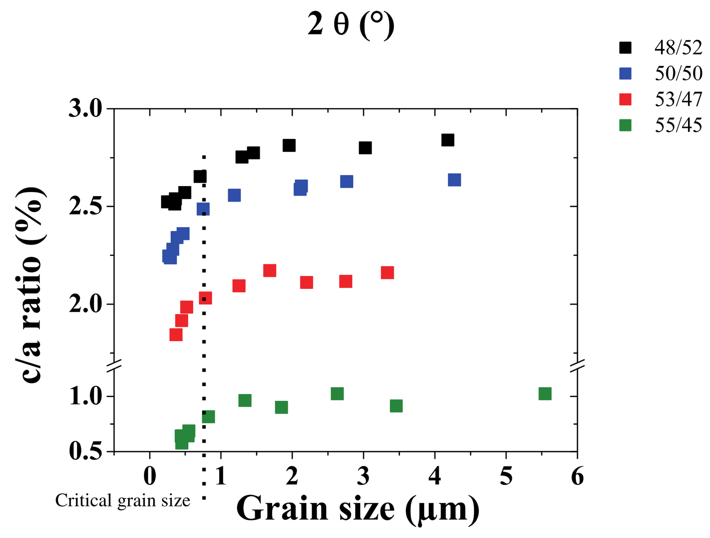
Change from complex domain structure to a simple lamellar domain structure by decreasing grain size.

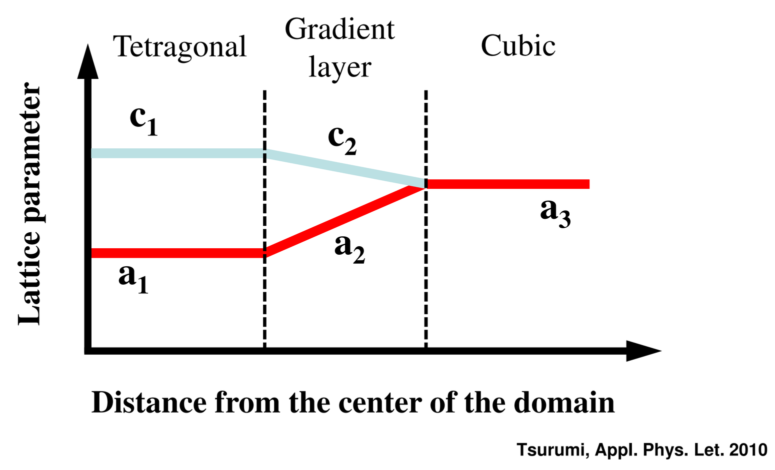
Crystal structure





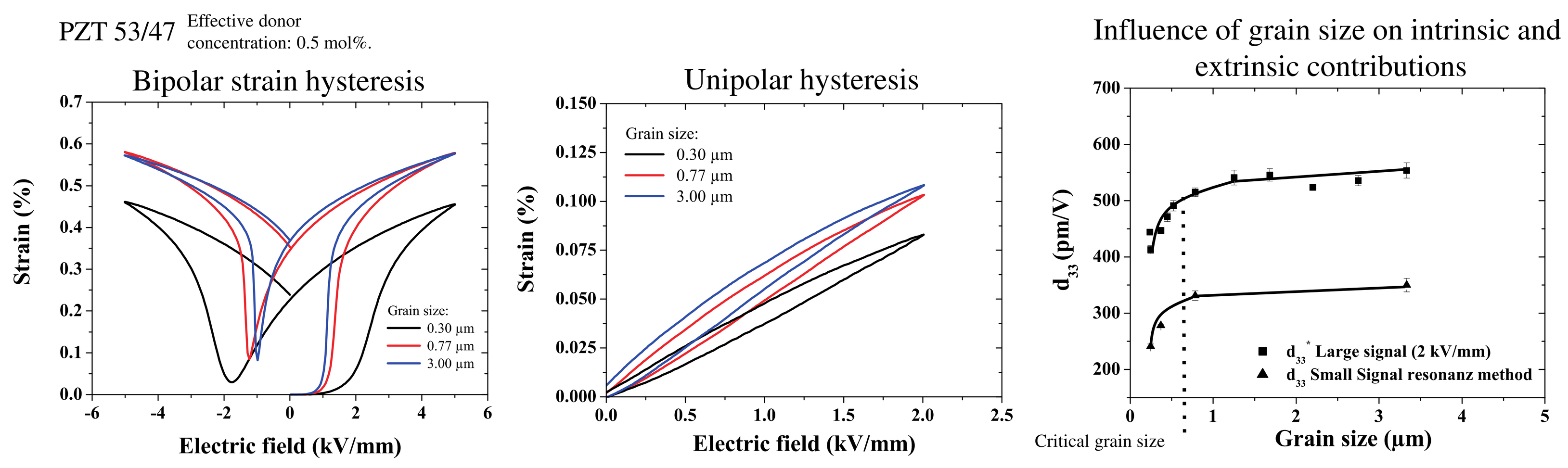




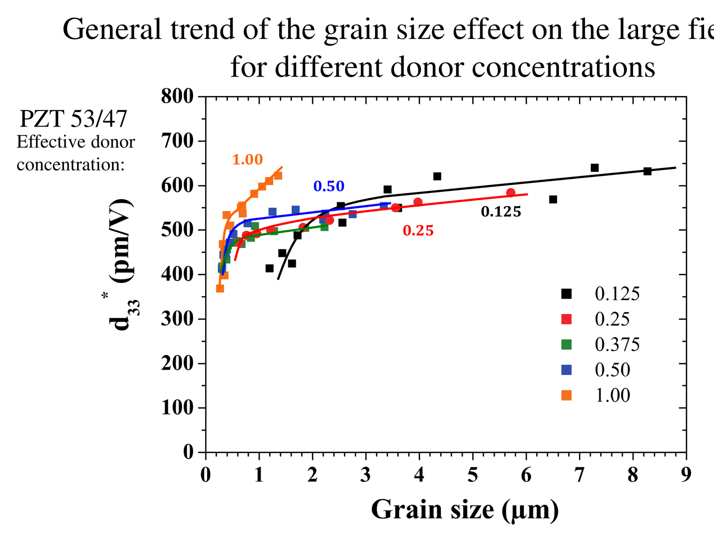


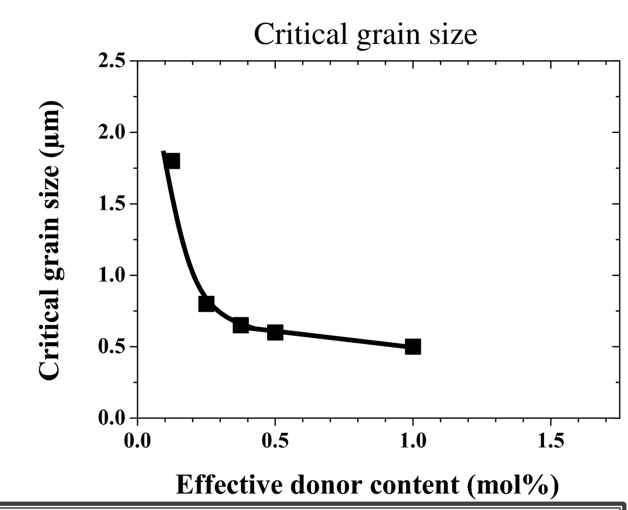
Decrease in tetragonal phase content and c/a-ratio by decreasing the grain size.

Electromechanical properties



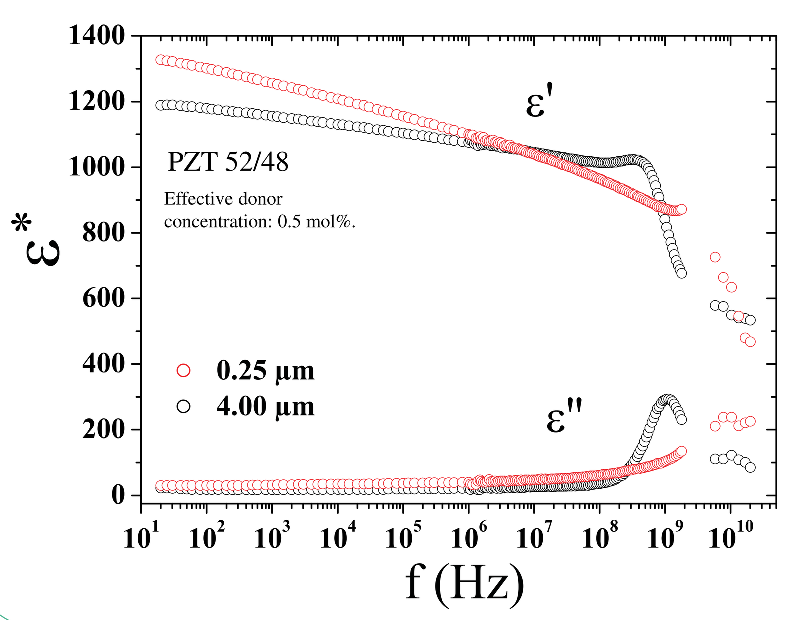
Decreasing the grain size of the PZT ceramics below a critical value leads to larger coercive fields and lower remanent strain. Both extrinsic and intrinsic contributions drop down at very low grain sizes.





The critical grain size is strongly influenced by the amount of effective donor dopant.

Frequency dispersion of the permittivity



The difference in the slope in the range between 10^1-10^8 Hz is probably caused by a different domain wall contribution to the permittivity. This implies a higher degree of disorder in the small grained sample.

The relaxation frequency is influenced by the domain size and is therefore shifted towards higher frequencies by decreasing grain size.

Acknowledgement: Dragan Damjanovic, Li Jin, EPFL Lausanne

Conclusions

A decrease in the grain size leads to a change in the complexity of the domain structure. The performed x-ray analysis shows a decreasing c/a-ratio for smaller grain sizes. This can be explained by an increase of the domain wall density and the pseudocubic structure close to the domain walls. This is in agreement with the frequency dependence of the permittivity showing a larger slope for a small grain size which implies a more disordered structure.

The change in the domain structure and lattice parameter cause a decrease in the electromechanical properties. Below a critical grain size the intrinsic and extrinsic contributions are strongly reduced. The critical grain size is affected by the effective donor content.