Field induced phase transition and formation of microdomains from polar nanoregions in lead free ferroelectrics

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Lead containing oxides with perovskite structure are widely used as sensors and actuators. Among those materials lead titanate zirconate $PbZr_{1-x}Ti_xO_3$ (PZT) and lead magnesium niobate-lead titanate, PMN-PT are the most prominent ones. The possible environmental hazard connected with lead has driven research of novel materials with comparable electrical and mechanical properties as PZT. For the dielectric properties of such materials the microstructure plays a crucial role. In PZT the domain structure diminishes to the scale of several nanometres in the vicinity of the morphotropic phase boundary, where the dielectric properties have a maximum [1].

Lead-free piezoelectric ceramics $(1-x-y)Bi_{0.5}Na_{0.5}TiO_3$-$xBaTiO_3$-$yK_{0.5}Na_{0.5}NbO_3$ ($0.05 \leq x \leq 0.07$ and $0.01 \leq y \leq 0.03$) (BNT-BT-KNN) have been synthesized by the mixed oxide route and sintering. Preliminary electromechanical characterization revealed a remarkable strain of approximately 0.4 % at an electric field of 8 kV/mm close to the boundary between two compositions with dominant ferroelectric and antiferroelectric properties [2, 3, 4].

In the unpoled state BNT-BT-KNN exhibits a pseudocubic symmetry in high resolution X-ray diffraction, performed at the MS synchrotron beamline at the SLS (Switzerland). However, high resolution neutron diffraction at the SPODI neutron diffractometer at the FRM II (Germany) showed superstructure reflections, which were indexed based on the tetragonal space group P4bm [5] and the rhombohedral one R3c [6]. No prominent domain structure as commonly seen in PZT polycrystals ceramics was observed in transmission electron microscopy (TEM) experiments. In contrast, electron diffraction revealed weak superlattice reflections in prominent zone axes. Temperature dependent Raman spectroscopy indicated a relaxor like behaviour, indicated by noncubic symmetry stable at the local scale and far above the Curie temperature. Therefore, in unpoled samples it can be deduced that ferroelectric distortions are present in polar nanoregions.

By applying an electric field *in situ* with synchrotron and neutron powder diffraction the former pseudocubic diffraction patterns show pronounced splitting of reflections and nanoscale domain structures become visible in TEM.

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