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Response of the ferroelectric domain structure of morphotropic PZT to the application of an electric field - in-situ Synchrotron X-ray diffraction

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The origin of the extremely high piezoelectric response of morphotropic ferroelectric lead zirconate titanate (PZT), $PbZr_{(1-x)}Ti_{(x)}O_3$, is still under discussion. Noheda et al. [1] proposed a monoclinic phase at the morphotropic phase boundary (MPB) as an explanation, via which a rotation of the polarization direction is possible. However, interpretation of X-ray data so far has not taken into account the strongly varying domain structure across the MPB. We have undertaken room-temperature and temperature-dependent synchrotron X-ray powder diffraction experiments with and without an applied electric field. A complete series of polycrystalline pellet samples across the MPB was analysed in transmission mode geometry in high-resolution and intermediate resolution image plate setup at B2, Hasylab Hamburg, Germany and also subjected to TEM imaging. The investigations show that the domain structure miniaturizes across the MPB down to nanodomains of 5-10nm width and as a consequence the diffraction patterns depict a strong increase in peak asymmetry as the tetragonal c/a-ratio decreases with increasing Zr content. These nanodomains appear in the same stability range as the proposed monoclinic phase. The existence of a monoclinic phase, however, is questioned by Jin et al. [2] for relaxor ceramics, assuming that it is just an effect of domain miniaturization and coherence in diffraction. The changes in domain structure have a dramatic influence on the poling behaviour of the material. While compositions at the edges of the MPB only show changes in domain orientation along the applied field, morphotropic samples exhibit strong changes in both lattice constants and intensities, accompanied by a strong increase in macroscopic strain. PZT 54/46 shows an increase in the intensity between the tetragonal 101 / 110 duplet under electric field and seems textured rhombohedral in-situ under 5kV/mm. The effects observed will be discussed in terms of reorientation of nanodomains through changes in domain configuration, stacking disorder, polarization rotation and possible phase transitions under electric field. The authors appreciate the financial support of the German Research Foundation (DFG) through the Sonderforschungsbereich 595 ''?Electric fatigue in functional materials'' and the virtual institute (VH-VI-102) of the Helmholtz Society.

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X-ray scattering study of crystallization of magnetron sputtered TiO_2 thin films

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In recent years, titanium dioxide films have been widely used in various fields because of their excellent chemical stability, mechanical hardness and optical transmittance with high refractive index. The photocatalytic activity of TiO_2 can result in the decomposition of organic compounds on the TiO_2 surface or the reduction of the contact angle between water and the TiO_2 surface after ultraviolet irradiation, i.e., in selfcleaning and antifogging effects, respectively. In the present work, a complex XRD study was performed on the films sputtered by dual magnetron on the glass substrates. A set of amorphous films with different thickness in the interval of 0.05 m to 2 m was investigated after deposition and then after isochronal annealing at temperatures up to 500 °C (step - 50 °C, time - 0.5 hour). The measurement was performed on two diffractometers - XRD7 (FPM-Seifert) and Philips X'Pert MRD in parallel beam setup, 2 q scan with angles of incidence 1-3° with collimators and Goebel mirror in the primary beam (Philips). It was found that the crystallization temperature is slightly below 250 °C with exception of two thinnest layers (0,1 μm and 0,054 μm) which were crystallized at 300 °C and 350 °C, respectively. Diffraction patterns show pure anatase phase for thinner films (up to 0,63 _m) and anatase with a small amount of rutile for thicker films. The crystalline films were studied in detail with the aid of different diffraction geometries. After annealing above the crystallization temperature no siginificant changes in peak intensities nor shapes have been observed up to the highest temperature. XRD line profile analysis shown that the line broadening is caused mainly by small crystallite size which was between 40 and 50 nm in most cases without significant differences between the films. Only weak textures were observed in the films. Detailed measurement of residual stresses was carried out on the Eulerian cradle with polycapillary in primary beam by the sin__ method for several different peaks. Linear dependence indicate absence of triple-axis stresses. For all crystalline films the tensile stress was about 200 MPa. Systematic strong strain anisotropy was detected. After annealing at 500 °C the stress values dropped down to zero. In addition, X-ray reflectivity curves were measured for all the samples after annealing at each temperature. The curves had to be fitted with a two-layer model. Very thin film on the surface can correspond to surface porous layer. An increase of surface roughness with increasing film thickness was observed. As expected, the roughness increased after crystallization of the films and it was increasing after next annealing as well. For the two thinnest films, other very thin layer was detected by the X-ray reflectivity. The layer was systematically reduced with annealing temperature.

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