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Nature of the morphotropic phase boundary (MPB) in lead zirconate titanate (PZT)

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Despite extensive studies the microstructure of the morphotropic phase boundary (MPB) in the ferroelectric material lead titanate zirconate $Pb(Zr_{1-x}Ti_x)O_3$ is still under discussion. Whereas some groups (Noheda et al. [1]) fitted diffraction data by monoclinic symmetry, other groups describe the MPB as composed of a complicated system of micro- and nanodomains [2]. The composition range from x = 0.40 to x = 0.55 is investigated by our group by a combination of X-ray diffraction and transmission electron microscopy (TEM) as a function of temperature and electric field [3]. Tetragonal $Pb(Zr_{0.45}Ti_{0.55})O_3$ and rhombohedral $Pb(Zr_{0.60}Ti_{0.40})O_3$ feature small microdomain widths coupled with a bimodal distribution. Around the morphotropic phase boundary an increase in microdomain widths associated with the formation of nanodomains is observed. In situ electric field synchrotron powder diffraction across the entire compositional range of the MPB shows changes in phase fractions and phase transitions dependent on the nanodomain content [4]. These observations are complemented by in situ studies of the domain structure under electric field in TEM [5]. Convergent beam electron diffraction (CBED) has been applied to elucidate the symmetry of the nanodomains. The results will be discussed together with calculations of the energy of formation of domains and on results obtained by electron spin resonance (EPR) [3].

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Phase transitions in MOX (M = Ti, V, Cr; X = Cl, Br)

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The compounds MOX (M = Ti, V, Cr; X = Cl, Br) crystallize in the FeOCl structure type with space group *P*mmn and lattice parameters *a* = 3.778, *b* = 3.355 and *c* = 8.027 Å for TiOCl at room temperature. All compounds go through phase transitions in dependence on temperature, which involve magnetic ordering as well as lattice degrees of freedom. TiOCl and TiOBr have attracted particular attention as one-dimensional (1D), S = 1/2 spin-chain compounds that are in a dimerized, spin-Peierls state at low temperatures (Seidel et al., 2003). Both compounds possess incommensurately modulated crystal structures at intermediate temperatures (van Smaalen et al., 2005). Here we give an overview of the temperature-dependent phase diagrams of TiOCl and TiOBr, and we discuss possible mechanisms for the normal-to-incommensurate and lock-in phase transitions (Schönleber et al., 2008). The pressure dependencies of the crystal structures and physical properties of these compounds are also discussed (Kuntscher et al., 2007). These results are analyzed in view of the phase transitions observed in VOCl and CrOCl.

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Local aspects of high-pressure phase transitions in ferroelectrics

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Ferroelectric materials in the perovskite structure (titanate, $KNbO_3$) undergo phase transformation under high pressure from tetragonal (orthorhombic) to cubic lattices. These phase transition are well documented from the long range order point of view, mainly through x-ray diffraction measurements but for the local point of view (which can differ from the average one) only few data are available[1]. In particular, the location of the Ti (Nb) atom in the cubic structure remains a crucial point in the real description of the material under high pressure. Recently we have performed x-ray absorption and/or diffuse scattering experiments under high pressure on $BaTiO_3$[2,3], $PbTiO_3$[4] and $KNbO_3$[3]. A coherent description of the cubic structure and of its evolution with pressure has been obtained, combining these two techniques. It has been shown that, at the transition, the Ti (Nb) atom remains off-centre but with a disordered displacement and that with increasing pressure, the off-centre shift was decreasing. For $BaTiO_3$ and $PbTiO_3$ the Ti atom is at the centre of the oxygen octahedron respectively at 10 GPa and 20 GPa, well above the tetragonal-cubic transition (2 and 12 GPa). For $KNbO_3$, the Nb atom remains off-centre up to the maximum pressure obtained during the experiment (22 GPa).

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