



## Sonderforschungsbereich 595

### Elektrische Ermüdung in Funktionswerkstoffen



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Short-range and long-range structural investigations of  
lead zirconate titanate (PZT) as a function of pressure,  
temperature and composition

Lead perovskites represent an important class of piezoelectric materials. Their dielectric and piezoelectric properties are known to be highly sensitive to stress induced by external elastic or electric fields and in this respect it is also very important to understand the effect of hydrostatic pressure on the phase diagram of these materials. The parent cubic perovskite structure presents two intrinsic instabilities: ferroelectric displacements and polyhedral tilting, which result in complex phase diagrams. Due to their high piezoelectric performances, lead titanate (PT) – lead zirconate (PZ) solid solutions,  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  (PZT) with  $x$  values of close to 0.48 are of particular interest. This composition lies on what is termed the morphotropic phase boundary (MPB), characterized by the presence of a monoclinic phase (space group Cm). In this phase, the polar axis can lie anywhere between the pseudocubic [111] and [001] directions, thus providing a possible origin for this high piezoelectric response.

Beginning with a composition of  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ , we have begun a detailed study of the pressure-temperature-composition phase diagram of the PZT system. We have studied PZT ( $0.80 \geq x \geq 0.20$ ) as a function of pressure and temperature by Raman spectroscopy, x-ray and neutron diffraction and dielectric measurements. In this region of the phase diagram, the stability range of the technologically-important monoclinic phase was determined and new low-symmetry phases were discovered. Careful Rietveld refinements using neutron diffraction data yield significantly better agreement factors using monoclinic models for the long-range structure of  $\text{PbZr}_{0.6}\text{Ti}_{0.4}\text{O}_3$  rather than the widely accepted rhombohedral symmetry. The spontaneous polarization was found to lie along the pseudocubic [112] direction instead of along the [111] direction. This polarization direction is shown to be adopted for a wide variety of compositions, temperatures and pressures. Neutron diffraction in particular enabled the compression mechanisms to be described, principally rotation and reduction of the spontaneous polarization and octahedral tilting. These two intrinsic instabilities of the perovskite structure can be directly probed by neutron diffraction following the intensities of certain reflections. A pseudocubic unit cell is observed just before the ferroelectric-paraelectric phase transition, irrespective of the composition, due to the competition between polar displacements and antiphase oxygen tilting. In order to investigate the ferroelectric displacements in this disordered material on a local level, combined high-pressure, high-temperature XAFS(Zr K edge)/X-ray diffraction experiments were performed. An abrupt decrease of the Debye Waller factor is observed at the ferroelectric paraelectric phase transition indicating a displacement of the Zr atom towards the centrosymmetric position on a local level in good agreement with the results obtained by diffraction.

In addition, it is found that the monoclinic phase, which is responsible for the exceptional piezoelectric properties of PZT, can be obtained at moderate pressures for non-morphotropic, Ti-rich  $\text{PbZr}_{0.40}\text{Ti}_{0.60}\text{O}_3$  and  $\text{PbZr}_{0.20}\text{Ti}_{0.80}\text{O}_3$ . The control of the stress state in thin films and ceramic materials may be used in a similar manner to pressure tuning to stabilize this technologically-important monoclinic form to design higher-performance materials. These results also contribute to the understanding of the observed higher performance of Ti-rich PZT materials in applications in which they are subjected to high-stress conditions (sonars, sensors, ultrasonic transducers, multilayered devices etc.).

Die Vorträge finden, wenn nicht anders angegeben, jeweils um **16:15**  
im Gebäude der Materialwissenschaften, Lichtwiese, Petersenstr. 23, **Raum 77** statt