Pressure-induced phase transitions in $0.9PbZn_{1/3}Nb_{2/3}O_3$-$0.1PbTiO_3$ up to 18.1 GPa

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Complex perovskite-type (ABO_3) ferroelectrics with Pb occupying the A site exhibit remarkable dielectric, electrooptic and electromechanical properties. The unique macroscopic properties are related to the existence of at least two types of cations in the same crystallographic position, which induces local atomic shifts and leads to the formation of dynamical nanoregions with coherent polar local structural distortions (polar nanoregions). One of the most attractive ferroelectric compounds from technological point of view and, at the same time, most challenging for theory, is the solid solution of $(1\text{-}x)Pb(Zn_{1/3}Nb_{2/3})O_3\text{-}xPbTiO_3$. Single crystals of $(1\text{-}x)Pb(Zn_{1/3}Nb_{2/3})O_3\text{-}xPbTiO_3$ show the strongest-ever observed direct and converse piezoelectric effect and are considered as the most promising materials for next-generation electromechanical sensors and transducers. The spontaneous polarization in this binary system is largest along the pseudocubic ⟨111⟩ direction, while the piezoelectric response is strongest along the pseudocubic ⟨001⟩ direction. $PbTiO_3$ (PT) is a normal ferroelectric that exhibits tetragonal structure at room temperature and pressure, whereas $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) is a relaxor ferroelectric with a polar rhombohedral structure at ambient conditions. Consequently, solid solutions of (1-x)PZN-xPT with a low x-value have rhombohedral symmetry, while those with a high x-value have tetragonal structure. The morphotropic phase boundary (MPB) is found to be near $x = 0.1$. The high degree of structural inhomogeneity makes it difficult to understand the structure-property relations in (1-x)PZN-xPT and in particular, to clarify the origin of the large piezoelectric effect: it may arise from heavy twinning and complex domain texture in the vicinity of MPB, or it may be related to the intrinsic structural complexity on the local scale. Previous high-pressure x-ray diffraction (XRD) studies combined with Raman spectroscopic analyses [1] demonstrated that pressure can help to understand the structural peculiarities of relaxor-based ferroelectrics. Hence, the aim of this study was analyze the pressure-induced structural transformations in 0.9PZN-0.1PT by synchrotron single-crystal XRD as a part of a larger study, involving high-pressure Raman scattering and high-precision in-house XRD.

Optically and chemically homogeneous single crystals of 0.9PZN-0.1PT with a mean size of ~ $8\times8\times4$ mm^3 were synthesized by the high-temperature solution growth method [2]. Synchrotron single-crystal XRD experiments were conducted at the F1 beamline of HASYLAB/ DESY, using a radiation of wavelength $\lambda = 0.5000$ Å and a MarCCD 165 detector. Plate-like specimens parallel to the cubic {100} planes were loaded in diamond-anvil cells of the Boehler-Almax design. A stainless steel gasket and a 4:1 methanol-ethanol mixture as a pressure-transmitting medium were used for the experiments up to 9.8 GPa, which is the hydrostatic limit of the alcohol mixture. To obtain hydrostatic conditions above 9.8 GPa, He was used as a pressure medium and rhenium was used for the gasket. Data were collected at a sample-to-detector distance of 100 mm with a step width of 0.5°, 80 frames per measurement, and an exposure time of 120 s per frame. The pressure was determined by the ruby-line luminescence method. Measurements on decompression verified the reversibility of the observed structural changes. Reciprocal-space sections were reconstructed from the raw data frames using the CRYSALIS™ Oxford Diffraction software.

The most important results from the synchrotron single-crystal XRD experiments are summarised in Figure 1. It is shown that polar nanoregions persist up to 4.0 GPa, which is the pressure at which the position of the lowest-wavenumber Raman peak, resulting from a Pb-localized phonon mode, reaches a minimum [2]. Near 4 GPa the pressure dependence of the position and width of the Raman peak related to Pb-O bond stretching within cubic {111} planes also rapidly change, indicating the development of antiferrodistortive order on the mesoscopic scale [3]. The appearance of a new set of *hkl* diffraction peaks with *h*, *k*, *l*, all odd (Miller indices refer to a cubic double-perovskite $Fm\bar{3}m$ unit cell) reveals a pressure-induced phase transition from a cubic to a non-polar rhombohedral phase, which is comprised of antiphase $a^-a^-a^-$ octahedral tilts (Glazer notation). Such a phase transition has been observed in all Pb-based relaxor ferroelectrics studied under pressure [1].

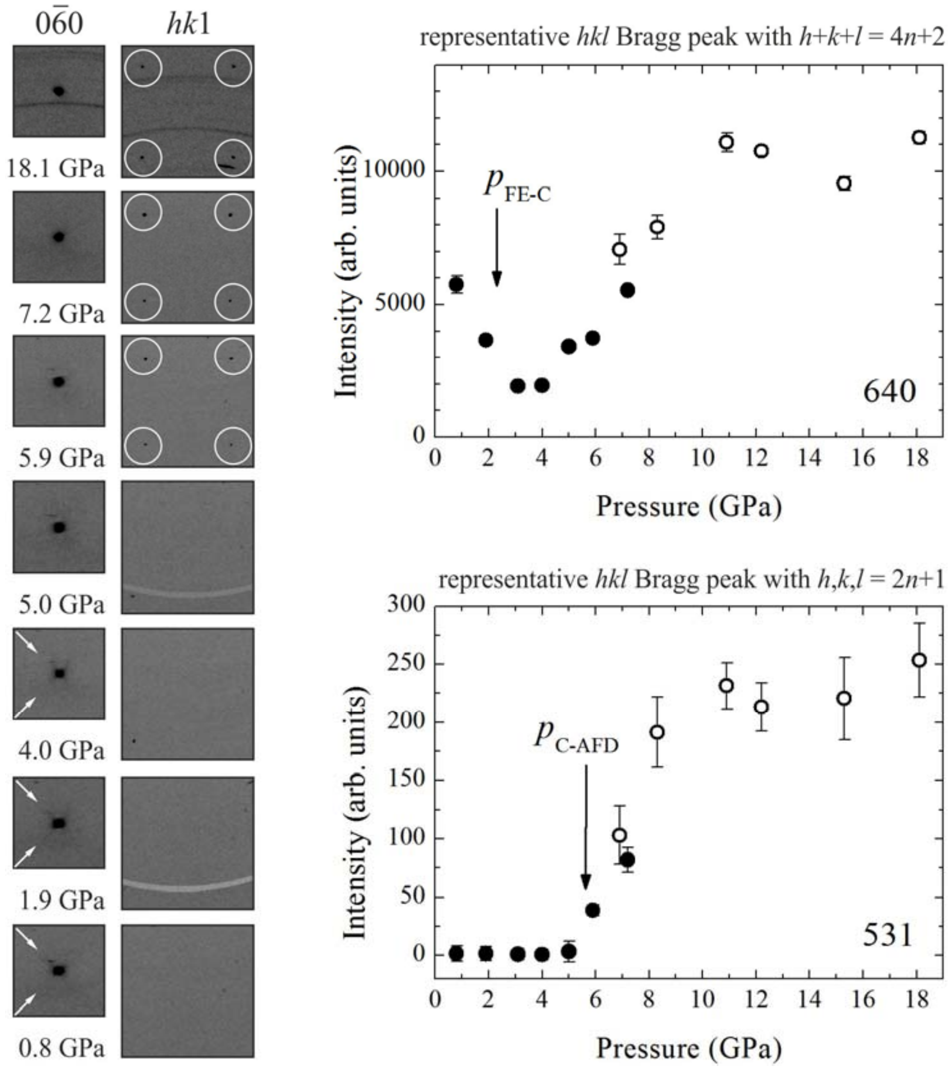

Figure 1: Reciprocal space layers of $0.9PbZn_{1/3}Nb_{2/3}O_3$-$0.1PbTiO_3$ reconstructed from synchrotron XRD data (left) and the pressure dependence of the integrated intensities of representative Bragg peaks with $h + k + l = 4n+2$ and $h, k, l = 2n + 1$ (right). The intensities are averages over the symmetry-equivalent peaks in the prototype cubic structure. The filled and open symbols correspond to measurements in methanol-ethanol and in He as pressure-transmitting media, respectively; the intensities were normalized to volume of the corresponding sample. The white arrows in the reciprocal layers mark the x-ray diffuse scattering along the cubic $\langle 110 \rangle^*$ direction, which is indicative of coherent polar cation shifts on the mesoscopic scale. The white circles mark the pressure-induced Bragg peaks with h, k, l all odd, which are indicative of long-range order of antiphase BO_6 tilts; p_{FE-C} in the upper plot denotes the phase transition pressure from a ferroelectric to a cubic state revealed by high-precision in-house XRD experiments [3], while p_{C-AFD} in the bottom plot denotes the pressure induced phase transition from a cubic to an antiferrodistortive rhombohedral state containing antiphase BO_6 tilts. All Miller indices are given for a double-perovskite cell with $Fm\bar{3}m$ symmetry.

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References

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