

## Thickness-induced structural transitions in three $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3/\text{PbZr}_{1-z}\text{Ti}_z\text{O}_3$ coherent superlattices ( $x/z = 0/0.2, 0.4/0.6, 0.6/0.8$ )

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The  $\text{PbZrO}_3$ – $\text{PbTiO}_3$  phase diagram displays several compounds of type  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ , all crystallizing in a structure close to the perovskite structure of  $\text{CaTiO}_3$ . At room temperature,  $x = 0$  corresponds to the orthorhombic antiferroelectric compound  $\text{PbZrO}_3$ . Ferroelectric compounds are, e.g., the rhombohedral ones  $\text{PbZr}_{0.8}\text{Ti}_{0.2}\text{O}_3$  ( $x = 0.2$ ) and  $\text{PbZr}_{0.6}\text{Ti}_{0.4}\text{O}_3$  ( $x = 0.4$ ) on the Zr-rich side of the morphotropic phase boundary (MPB;  $x \approx 0.5$ ), and the tetragonal ones  $\text{PbZr}_{0.4}\text{Ti}_{0.6}\text{O}_3$  ( $x = 0.6$ ) and  $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  ( $x = 0.8$ ) on its Ti-rich side. All of them can be considered a derivation from a cubic prototype perovskite with a lattice parameter around 0.4 nm. The specific structural (crystal structure, lattice parameters, antiferroelectric/ferroelectric domains) and electrical properties are the result of various rather small but most significant deviations from this prototype structure. Corresponding small ion shifts result in dielectric dipoles, and in deviations from the cubic symmetry. As will be shown here, the compounds, however, still remember their cubic prototype and therefore can be forced into a different phase by appropriate constraints like strain. From a combination of different of these compounds within one and the same superlattice new or modified properties and an insight into microstructure-property relations, like, e.g., the impact of interfaces, can be expected, which at the end should allow for a tuning of the properties.

$\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3/\text{PbZr}_{1-z}\text{Ti}_z\text{O}_3$  superlattices with (001) orientation (in cubic notation) of the following types were prepared by pulsed laser deposition (PLD) at elevated substrate temperatures, e.g., 575 °C, in 10...30 Pa oxygen. For experimental details, see [1-3].

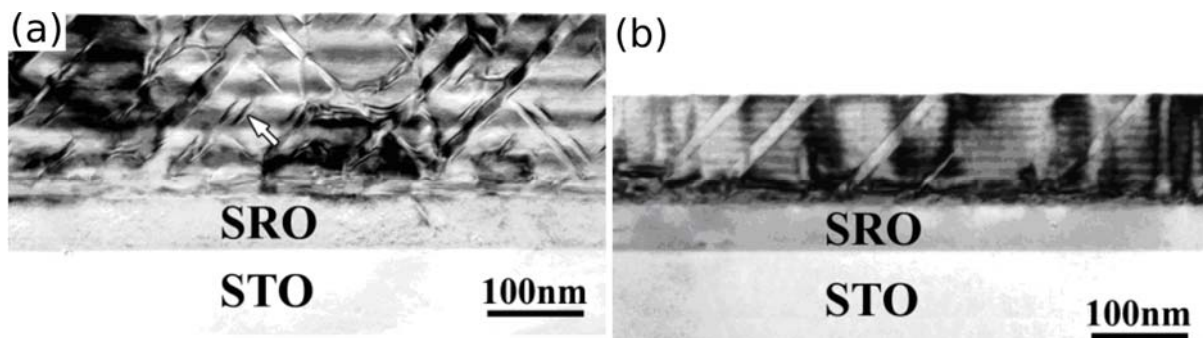
- (i)  $\text{PbZr}_{0.4}\text{Ti}_{0.6}\text{O}_3 / \text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  ( $x/z = 0.6/0.8$ ), i.e. tetragonal/tetragonal (“tet/tet”),
- (ii)  $\text{PbZr}_{0.6}\text{Ti}_{0.4}\text{O}_3 / \text{PbZr}_{0.4}\text{Ti}_{0.6}\text{O}_3$  ( $x/z = 0.4/0.6$ ), i.e. rhombohedral/tetragonal,
- (iii)  $\text{PbZrO}_3 / \text{PbZr}_{0.8}\text{Ti}_{0.2}\text{O}_3$  ( $x/z = 0.0/0.2$ ), i.e. orthorhombic/rhombohedral,

in this way receiving both (i,ii) ferroelectric/ferroelectric and (iii) antiferroelectric/ferroelectric superlattices. Circular platinum top electrodes of, e.g., 0.15 mm diameter were sputtered through a shadow mask. The thickness of the individual layers ( $2 \text{ nm} < t < 50 \text{ nm}$ ) and the overall thickness of the superlattices ( $50 \text{ nm} < T < 200 \text{ nm}$ ) were varied in a systematic way. All superlattices were grown on (100)-oriented  $\text{SrRuO}_3$  (SRO) bottom electrodes, which were also grown by PLD, onto (100)-oriented  $\text{SrTiO}_3$  (STO) vicinal single-crystal substrates with a miscut of  $0.1^\circ$  in order to achieve step-flow growth. As a rule, the first layers grew pseudomorphically, whereas strain relaxation can be expected at higher thickness. The superlattices were structurally investigated by (HR)TEM, (RSM-)XRD, and AFM. The ferro- and antiferroelectric properties were macroscopically characterized by electrical measurements (polarization-field, capacitance-voltage), and locally by piezoresponse force microscopy (PFM).

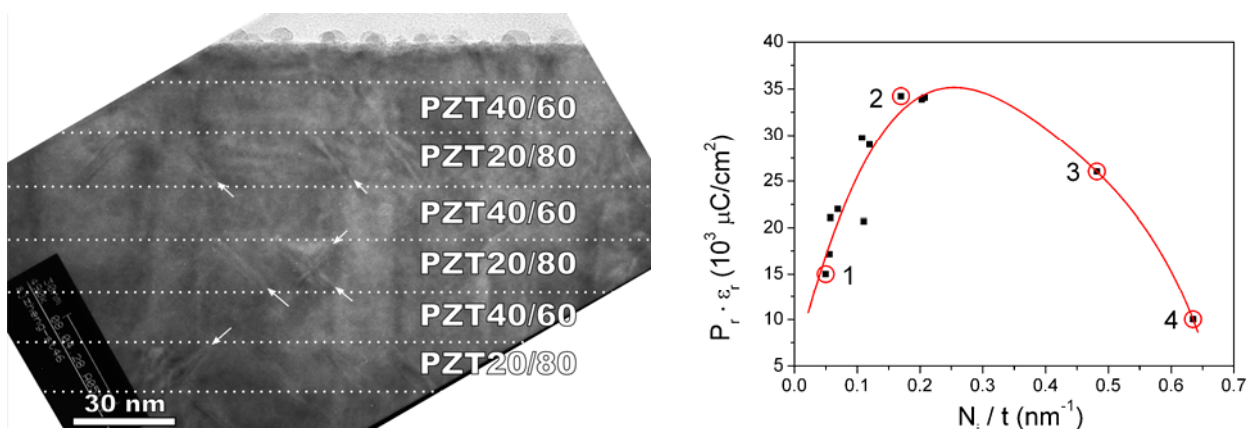
In all three types of superlattices, a thickness-dependent and obviously strain-related structural transition was observed by (HR)TEM and (RSM-)XRD below a certain critical

thickness  $t_C$  of the individual layers (see Fig. 1).  $t_C$  was between 5 nm and 9 nm in all cases, slightly depending on the type of superlattice. Of the two constituents, in all cases the thermodynamically less stable one (the one with the lower Curie temperature) underwent the transition, whereas the thermodynamically more stable one prevailed. As a consequence, the electrical properties of the superlattices significantly changed (see Fig. 2, right), either quantitatively or even qualitatively. For example, in type-(iii) superlattices, the structural transition of  $\text{PbZrO}_3$  (from the orthorhombic to a rhombohedral structure) was accompanied by an antiferroelectric-to-ferroelectric transition [3].

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4. Contributions by A. Lotnyk (XRD), I. B. Misirlioglu (thermodynamic calculations), L. Pintilie (electric measurements), G. Le Rhun (PFM), B. Rodriguez (PFM), and M. A. Schubert (XRD), are gratefully acknowledged. Work supported *via* SFB 762.



**Figure 1.** Comparison of two  $\text{PbZr}_{0.4}\text{Ti}_{0.6}\text{O}_3$  /  $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  “tet/tet” superlattices. (a)  $t = 20$  nm,  $T = 200$  nm, with a complex pattern of  $90^\circ$ -a-c domains. (b)  $t = 6$  nm,  $T = 110$  nm, with a uniformly extending, rather regular pattern of  $90^\circ$ -a-c domains indicating a common strain state (uniform lattice) of all layers independently on composition. (Images from [1]).



**Figure 2.** (Left) HRTEM micrograph of a  $\text{PbZr}_{0.4}\text{Ti}_{0.6}\text{O}_3$  /  $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  “tet/tet” superlattice showing the presence of  $90^\circ$ -a-c domains mainly in the  $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  layers (white arrows). (Right) Dependence of the product  $P_r \cdot \epsilon_r$  of remanent polarisation and dielectric permittivity on the reciprocal thickness of the individual layers. The highlighted point No. 1 corresponds to Figure 1(a), whereas point No. 2 corresponds to Figure 1(b). (Images from [1]).