

domains in an isotropic arrangement. There are also other weaker patterns with axial symmetry about the Bragg rod. Application of a field brings about large changes. The diffuse scattering becomes much more diffuse, apparently involving a migration closer to the film Bragg peak, evidence of an increased spread in domain size and domain disorder. After removing the field the domain distribution does not relax back to the initial state, presumably reflecting the influence of domain wall pinning in stabilizing a field-induced domain geometry.

Keywords: synchrotron X-ray scattering, perovskite oxides, thin ferroelectric films

### P11.11.45

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#### Effect of doping on the poling behaviour of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ under electric field

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Lead zirconate titanate  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$  (PZT  $x/1-x$ ) ceramic is one of the most important perovskite ferroelectric material for application in various sensors and actuators. Especially, the solid solution composition located near the rhombohedral-tetragonal morphotropic phase boundary (MPB) possesses eminent piezoelectric characteristics and is widely utilized in a donor or acceptor doped modification with improved electrical properties. Here in particular samples doped with either lanthanum or iron of compositions at the morphotropic phase boundary are investigated, as they depict highest strain values under electric field compared to single phase tetragonal ( $P4mm$ ) or rhombohedral ( $R3m$ ) compositions. We have been able to show changes in phase fractions, domain structure and phase transitions under electric field dependent on the nanodomain content in recent work for undoped PZT [1,2,3,4]. To extend the analysis of in-situ data under electric field we have performed full pattern Rietveld analysis of diffraction patterns recorded in transmission mode in-situ under electric field at the beamline B2 at Hasylab in Hamburg. The investigation of the domain structure and its alteration under the influence of an applied electric field was of special interest. The results can be correlated with undoped PZT with respect to the alteration of the properties and the reaction to an electric field. We can therefore say that already very small amounts of dopants can have a very pronounced effect on the behaviour of PZT under applied electric field.

[1] L. A. Schmitt et al., *J. Appl. Phys.* **101**, 074107 (2007).

[2] K. A. Schoenau et al., *Phys. Rev. B* **75**, 184117 (2007).

[3] R. Theissmann et al., *J. Appl. Phys.* **102**, 024111 (2007).

[4] K. A. Schoenau et al., *Phys. Rev. B* **76**, 144112 (2007).

Keywords: lead zirconate titanate, X-ray diffraction, domain structure

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#### Structural study of ferroelectric/relaxor multilayers of the $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 - (x)\text{PbTiO}_3$ family

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The complex oxide ferroelectric materials  $[(1-x)\text{PMN} - x\text{PT}]$  have generated a great deal of interest due to their exceptional electromechanical coupling in single crystal form, thus their fabrication as thin films is important for practical applications. Since the microscopic origin of these exceptional piezoelectric properties seems to be directly linked to the complex nanostructure of the material, it is fundamental to understand the influence of strain in these materials, when they are in the form of films and heterostructures. In order to investigate the effect of strains and interactions between the relaxor PMN and the ferroelectric PT, we grew a series of  $[\text{PMN}(1-x)\text{L}/\text{PTxL}]_{10}$  superlattices [1] on buffered MgO substrates, with  $x$  varying between 0.2 and 0.9; the modulation period  $L$  nominally is 150Å. Here we report on both the out-of-plane and the in-plane structures of PMN and PT layers as a function of  $x$ . We show the interlayer structural coupling between the relaxor PMN and the ferroelectric PT in PMN/PT superlattices. The effects of strains in such superlattices generate structural patterns in these materials that are not ordinarily achievable in thin films, and can also provide a way to control the polarization axis in very thin ferroelectric layers. The presence of  $a_1$  and  $a_2$  domains is expected since this type of domain structure is usually observed in PT thin films. These polydomain patterns result from the strain relaxation at the substrate/ferroelectric film interface and are thickness dependent [2]. To our knowledge, it is the first time that this domain structure is observed in superlattices.

[1] H. Bouyanfif et al. *Phys. Rev. B* **76**, (2007).

[2] K. S. Lee et al. *J. Appl. Phys.* **87**, 11, 8035 (2000) ; K. S. Lee, et al. *J. Appl. Phys.* **90**, 8, 4095 (2001).

Keywords: perovskite, multilayers, ferroelectrics and related materials

### P11.11.47

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#### Short and long-range order structure in the $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$ ( $x = 0.20$ and $0.30$ ) ferroelectric ceramics

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Lanthanum-doped lead titanate ceramics ( $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$  or  $\text{PLTx}$ ) is a family of ferroelectric compound which have been studied in detail due to their interesting technological properties. The isomorphic substitution of Pb in  $\text{PbTiO}_3$  by La atoms induces significant changes in its electrical properties. We have studied the long and short-range order structure of the PLT and its dependence with the normal and relaxor behaviour presented on PLT ceramics with  $x=0.20$  (normal ferroelectric) and  $x=0.30$  (relaxor ferroelectric) by in-situ XRD and XAS techniques above and below  $T_c$  and  $T_m$  respectively. The PLT20 XRD patterns were measured on a Rigaku Denki powder diffractometer with geometry  $2\theta$ , a rotating anode X-ray source (Cu  $K\alpha$ ). The PLT30 XRD patterns were performed at LNLS (Brazilian Synchrotron Light Laboratory). To study the behaviour of the phases as a function of the temperature, some peaks of the PLT30 sample were selected and measured varying the temperature with a step of 10

K around the transition temperature. In order to determine precisely the structure at high and low temperatures, Rietveld refinements of a complete  $2\theta$  range were performed on the patterns collected below and above the transition temperature either for PLT20 or PLT30. The temperature dependence of the relative dielectric permittivity was also performed. From the final Rietveld refinements it was observed important structural trends and it was possible to determine the range where the ferroelectric-to-paraelectric phase transition takes place. The results observed with the XRD refinements agree with that one observed by electric measurements. Structural details, in terms of short and long-range order, are presented and the correlation between the XRD and XANES/EXAFS data is discussed.

Keywords: Rietveld structural refinement, perovskite structures, phase transitions and structure

**P11.11.48**

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**Different models for the polar nanodomain structure of PZN and other relaxor ferroelectrics**

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Computer simulations have been carried out to test the recently proposed model [1] for the nano domain structure of relaxor ferroelectrics such as lead zinc niobate (PZN). In this recent model it was supposed that the polar nanodomains are three dimensional, that the observed diffuse rods of scattering originate from the boundaries between domains and that the Pb displacements may be directed along  $\langle 100 \rangle$ ,  $\langle 111 \rangle$  or  $\langle 110 \rangle$ . This is in marked contrast to our previously published model [2] which described the polar domains as thin plates with Pb displacements confined to  $\langle 110 \rangle$  directions within the essentially 2D domains. The present results confirm that  $\langle 100 \rangle$  and  $\langle 111 \rangle$  types of Pb displacement are viable possibilities but the number of domain boundaries required to produce sufficiently strong diffuse rods of scattering means that individual domains cannot be described as three dimensional and must still be relatively thin. The current work has been carried out with no direct involvement of the B-site cation ordering that many workers assume is necessary to understand the formation of the polar nanodomains. While it may be true that the B-site cation distribution could provide an underlying perturbation field that might ultimately limit the extent of any polar domain, it is certainly not necessary to produce the observed scattering effects. In an attempt to establish which of the now available models is correct the behaviour of each in an electric field has been explored.

[1] Pasciak, M., Wolcyrz, M. & Pietraszko, A. (2007). *Phys. Rev.* B76, 014117.

[2] Welberry, T.R., Goossens, D.J. & Gutmann, M.J. (2006). *Phys. Rev.* B74, 224108.

Keywords: diffuse scattering, relaxor ferroelectrics, PZN

**P11.11.49**

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**Structural aspects of the effect of NaNbO<sub>3</sub> substitution on quantum paraelectric behavior of CaTiO<sub>3</sub>**

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Several perovskite titanates like SrTiO<sub>3</sub>, CaTiO<sub>3</sub> (CT), EuTiO<sub>3</sub>, La<sub>1/2</sub>Na<sub>1/2</sub>TiO<sub>3</sub> and KTaO<sub>3</sub> are known to exhibit unusual phenomenon of quantum paraelectricity. For these materials, the dielectric constant increases with decreasing temperature but does not show a peak corresponding to a ferroelectric (FE) or antiferroelectric (AFE) transition. Instead, their dielectric constant becomes temperature independent at very low temperatures. This has been attributed to the suppression of FE/AFE transition due to zero point quantum fluctuations of the lattice. We have recently shown that substitution of Pb<sup>2+</sup> in CT can stabilise AFE phase with negative Curie-Weiss temperature [1]. In this work, we present evidence for a phase transition at low temperatures in the system (1-x)CaTiO<sub>3</sub>-xNaNbO<sub>3</sub> (CT-xNN), as a result of Na<sup>+</sup> and Nb<sup>5+</sup> substitutions at Ca<sup>2+</sup> and Ti<sup>4+</sup> sites. NaNbO<sub>3</sub> substitution leads to a dielectric anomaly superimposed over a continuously rising paraelectric background of pure CT. This anomaly is characterized by a negative Curie-Weiss temperature indicating an AFE transition. Temperature dependent XRD studies reveal the appearance of weak superlattice reflections below the AFE transition temperature. One of the unit cell parameters of the AFE phase is found to be 6 times that of the paraelectric phase. The paraelectric to AFE transition is shown to be first order as evidenced by a discontinuous change in the unit cell parameters. Our previous study on Pb<sup>2+</sup> substituted CT [1] and the present study on CT-xNN suggest that CT is an incipient AFE. We also show that the mixed CT-xNN system exhibits morphotropic phase boundary like characteristics [2].

**References:**

[1]. A. Chandra et al, *J. Phys.: Condens. Matter* **18**, 2977 (2006).

[2]. S. Tripathi et al, *Phys. Rev. B* **77**, 052104 (2008).

Keywords: quantum paraelectric, morphotropic phase boundary, antiferroelectric

**P11.11.50**

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**Synthesis and characterization of Bi(Ni<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub>**

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Ferroelectric lead zirconate titanate is widely used as integral parts of electrical devices due to the high dielectric and electromechanical properties. However, the toxicity of lead oxide results in serious environmental problems and hence alternative compounds free from lead are urgently under development. Since Bi<sup>3+</sup> ion has the same electronic structure as the Pb<sup>2+</sup> ions, Bi-containing perovskites are promising candidates for lead-free ferroelectric ceramics. Bi(Ni<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub>, BNT, ceramic was

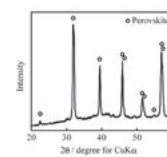


Fig. 1. Powder x-ray diffraction pattern of the BNT ceramic synthesized at 6 GPa, 1000 °C.

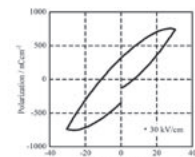


Fig. 2. P-E hysteresis loop of the BNT ceramic.