

coupled below the ferroelectric temperature $T_{FE} = 28$ K. While below T_{FE} it is known that Tb-spins are induced to order with $\tau^{Tb} = \tau^{Mn}$, below 7 K we find that τ^{Tb} and τ^{Mn} lock-in to rational values of $3/7 b^*$ and $2/7 b^*$, respectively, and obey the relationship $3\tau^{Tb} - \tau^{Mn} = 1$. We explain the novel matching of Tb and Mn wave vectors within the frustrated ANNNI model coupled to a periodic external field produced by the Mn-spin ordering. The $\tau^{Tb} = \tau^{Mn}$ behavior is recovered when Tb magnetization is small, while the $\tau^{Tb} = 3/7$ regime is stabilized at low temperatures by a peculiar arrangement of domain walls in the ordered state of Ising-like Tb spins. Our phase diagram not only reproduces the experimentally observed value of τ^{Tb} but also explains magnetic ordering for R-spins that is realized for R = Dy and Ho.

Keywords: magnetic perovskite materials, magnetic phase transitions, ferroelectricity

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Structure of Sr and Ti codoped LaAlO_3 perovskite

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Rare-earth aluminates, LnAlO_3 (Ln is abbreviated for lanthanide metals such as Ln = La, Ce, Pr, Nd, Pm, Sm, Eu and Gd) are known to possess excellent dielectric properties. In particular, the sintered samples of $(\text{La}_{1-x}\text{Sr}_x)(\text{Al}_{1-x}\text{Ti}_x)\text{O}_3$ perovskite-type solid solution have higher quality factors than that of LaAlO_3 , peaking $Q_f = 165000$ MHz at $x = 0.2$ ¹⁾. This paper aims at clarifying the structure-property relation in the solid solution. Single crystals of $x=0.005$ and 0.20 were grown by the floating-zone method²⁾ and examined by the single-crystal x-ray diffraction method. The crystals possessed weak but significant intensities at the reciprocal lattice points forbidden for the space group $R-3c$ which is commonly assumed for the rhombohedral distortion of the perovskite as in LaAlO_3 . The present study revealed that the crystals ($x=0.005$ and 0.2) belong to $R-3$ which accommodates two crystallographically independent octahedral sites for Al(Ti). Ti atoms are preferentially concentrated on the larger Al(Ti)O₆ octahedra. The selective distribution of Ti provides in the $R-3$ structure a less distorted Al(Ti)-O-Al(Ti) bond angle than that in $R-3c$. This is consistent with the physical property that the Sr and Ti codoped compounds have higher Q_f than the pure LaAlO_3 . Discussion will be given on the reasons why the symmetry of Sr and Ti codoped crystals differs from the pure LaAlO_3 ³⁻⁴⁾, the end member of the 'solid solution'.

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Keywords: perovskite, new rhombohedral, distortion

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Mobile oxygen form and structural stability of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-y}$ perovskites

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Using thermogravimetry with mass spectrum analysis, low and high-temperature X-ray powder diffraction $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-y}$ solid solutions with perovskite-related structure were investigated. From -190 °C and up to room temperature under heating of samples in vacuum perovskite structure preserved. Oxygen loss under heating of samples ($0 \leq x \leq 1$) in air and in vacuum ($x < 0.75$) under temperature of synthesis (1200 °C) leaved the structure unaltered, however, resulted in increase of unit cell volume. Heating in vacuum of compositions $x \Rightarrow 0.75$ resulted in vacancies-ordered phase formation. These structural changes (increase of unit cell parameter, oxygen vacancies ordering) are reversible and reoxidation leads to restoring of initial oxide parameters in process of cooling down in air or in a second heating in air of "vacuum-processed" samples. Loss of oxygen for initial samples under heating and reoxidation process for "vacuum-processed" samples occurred at the same temperature about 400 °C. Amount of emitted oxygen under heating in vacuum and in helium atmosphere increased as compared with those of realised under heating in air.

Keywords: perovskites, high-temperature X-ray diffraction, mobile oxygen form

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X-ray study of the impact of a weak electric field on the domain structure in PbTiO_3 thin films

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Thin films of PbTiO_3 (PTO) deposited on SrTiO_3 (STO) single crystal (001) faces have been studied by SR X-ray scattering to investigate domain size and orientation as a function of film thickness and the impact of a weak electric field. The nearly perfect lattice match between cubic STO and the ab -plane of tetragonal PTO ensures that the polar PTO c -axis will be well aligned in the growth direction of the film, favouring the formation of c -oriented domains. Thin films of PTO in the thickness range 207 - 24.5 Å deposited by RF magnetron sputtering on insulating STO substrates were studied, using a sample holder allowing the application of an electric field, about 4000 V/cm, onto the sample along the polar axis. In order to study the field effects on the domain structure, scans of reflections $0\ 0\ l$, $h\ 0\ l$ and $0\ k\ l$ were made without field, with field, and again without field after a period with the field turned off. Reconstructions of the diffuse scattering display a surprising complexity which is different for various film thicknesses. The field effects are most prominent for the thickest film (50 uc). Before exposure to the field the major part of the diffuse intensity describes an annular ring relating the average period of the

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

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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.

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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 $[\text{PMN}(1-x)\text{L}/\text{PT}x\text{L}]_{10}$ 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.

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Keywords: perovskite, multilayers, ferroelectrics and related materials

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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 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 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 2θ , 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