

P.11.12.9*Acta Cryst.* (2005). **A61**, C400**Local Symmetry in $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ -Ceramics**Roland Schierholz^a, Ralf Theissmann^a, Hans Kungl^b, Hartmut Fuess^a,
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The symmetry of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ in the region of the morphotropic phase boundary is still under debate. Noheda *et al.* [1] claimed the existence of a monoclinic phase. In contrast to this Jin *et al.* [2] showed for relaxor ceramics that, if the width of tetragonal microdomains is smaller than the diffraction coherence length, the measured crystal lattice constants are of monoclinic symmetry.

With convergent-beam electron diffraction (CBED) very small volumes can be examined. So crystal symmetry can be investigated on single domains. To distinguish the most probable phases with space group symmetry $P4mm$, $R3m$ and Cm , just one zone-axis is needed. At most two projected CBED-patterns of neighbouring domains are necessary. The method will be explained by the use of simulated and experimental CBED-patterns.

[1] Noheda B., Gonzalo J.A., Cross L.E., Guo R., Park S.E., Cox D.E., Shirane G., *Phys. Rev. B*, 2000, **61** 8687. [2] Jin Y.M., Wang Y.U., Khachatryan A.G., Li J.F., Viehland D., *Phys. Rev. Lett.*, 2003, **91**, 197601.

Keywords: convergent-beam electron diffraction, crystal symmetry, microdomains

P.11.12.10*Acta Cryst.* (2005). **A61**, C400**Local Order in the PSN, PST and PSNT Ferroelectric Relaxors**Adam Pietraszko, Marek Paściak, Marek Wołczyr, *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, ul. Okólna 2, 50-950 Wrocław, Poland.* E-mail: adam@int.pan.wroc.pl

Diffuse X-ray scattering studies were performed for as grown $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$ - PSN, $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ - PST and $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.2}\text{Ta}_{0.3})\text{O}_3$ - PSNT which belong to the ferroelectric relaxors family of complex $\text{Pb}(\text{B}^{3+}_{0.5}\text{B}^{5+}_{0.5})\text{O}_3$ perovskites in which the degree of order could be controlled by the thermal history [1]. In the disordered state the ferroelectric relaxors consist of a nonpolar matrix ($Pm3m$ space group) that contains nanosize chemical domains and polar nanodomains [2,3]. The crystal structures of PSN, PST and PSNT were studied on single crystals at several temperature points in the range from 300 to 550 K by means of a four-circle single crystal diffractometer equipped with CCD area detector. Diffuse streaks and superstructure reflections were found in PSN, PST and PSNT crystals. The diffraction patterns of the disordered structures for the relaxors of the 1:1 composition were simulated using the DISCUS program [4] and compared with those obtained experimentally.

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[1] Cross L.E., *Ferroelectrics*, 1994, **151**, 305. [2] Baba-Kishi K.Z., Woodward P.M., Knight K., *Ferroelectrics*, 2001, **261**, 21. [3] Takesue N., Fujii Y., Ichihara M., Chen H., Tatemori S., Hatano J., *J. Phys.: Condens. Matter.*, 1999, **11**, 8301. [4] Proffen, Th., Neder, R. B., *J. Appl. Cryst.*, 1997, **30**, 171.

Keywords: local order, ferroelectric relaxor, diffuse scattering

P.11.12.11*Acta Cryst.* (2005). **A61**, C400**In-situ Electric Field Synchrotron Diffraction of $\text{PbZr}_x\text{Ti}_{(1-x)}\text{O}_3$ Microdomains**Hartmut Fuess^a, Kristin A. Schoenau^a, Ljubomira Schmitt^a, Michael Knapp^a, Ralf Theissmann^a, Hans Kungl^b, ^a*Institute for Materials Science, Darmstadt University of Technology.* ^b*Institute for Mechanical Engineering, Karlsruhe University of Technology, Germany.* E-mail: hfuess@tu-darmstadt.de

The structure of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ at its morphotropic phase boundary (MPB) and the influence of electric field on the domain structure in this area have been the subject of controversy. While Noheda *et al.* [1] proposed a monoclinic "bridging" phase at the MPB without

considering the real structure, Jin *et al.* [2] describe an adaptive phase of tetragonal microdomains in relaxors, which are not resolvable with X-rays and therefore only appear to be of monoclinic symmetry.

In this work, a correlation is drawn between these two models, and the variation of the domain structure with composition and electric field is investigated. Rietveld refinement and analysis of ex-situ and in-situ electric field high-resolution synchrotron X-ray diffraction data of polycrystalline pellets (~60µm), measured in transmission geometry, and TEM studies indicate various changes in domain structure across the MPB. A lowering of the domain wall energy by a decrease in *c/a*-ratio of the tetragonal phase with lower Ti fraction leads to a simultaneous increase in content of microdomains – the adaptive phase, which has a tremendous influence on the poling behaviour of the material.

[1] Noheda B., Gonzalo J.A., Cross L.E., Guo R., Park S.E., Cox D.E., Shirane G., *Phys. Rev. B*, 2000, **61**, 8687. [2] Jin Y.M., Wang Y.U., Khachatryan A.G., Li J.F., Viehland D., *Phys. Rev. Lett.*, 2003, **91**, 197601.

Keywords: high-resolution X-ray diffraction, in-situ electric field, ferroelectric microdomains

P.11.12.12*Acta Cryst.* (2005). **A61**, C400**Analysis of the Crystalline Phases of PLZT doped with Nd, Ho, Er, Tm, Yb**Yvonne P. Mascarenhas^a, Leandro D. Santana^a, Ducinei Garcia^b, Mirta M. Caraballo^a, ^a*Institute of Physics of São Carlos, USP, São Carlos, SP, Brazil.* ^b*Department of Physics, UFScar, São Carlos, SP, Brazil.* E-mail: yvonne@if.sc.usp.br

The addition of La to PZT improves densification, transparency and electro-optical properties. To further improve those qualities samples of PLZT doped with Yb, Ho, Tm, Er and Nd were produced and characterized by XRD (Rigaku-Denki rotating anode source RU-200 B, $\lambda = 1.5408$, $i = 100\text{mA}$, $V = 50\text{kV}$, θ - 2θ scan from 15 to 120°, step 0.02°, time = 5sec, room temperature, Rietveld Method, GSAS package of programs) Samples of PLZT 65/35 and 9% La were produced with 1, 2, 4% of Yb and syntherized at room temperature. They presented systematically a mixture of Rhombic ($R3cH$) and tetragonal ($P4/mm$) phases. It was observed that less than 1% Yb incorporated with the excess forming a third phase of $\text{Zr}_2\text{Yb}_4\text{O}_{12}$. For this reason PLZT samples containing only 1% of rare earth were prepared and syntherized at high temperature. It was observed the formation of only the rhombohedral phase. The rare earth ions occupied both sites A and B of the perovskite structure with *sof* respectively of 0.099 and 0.0232 for Nd, 0.0102 and 0.0130 for Ho, 0.0179 and 0.0164 for Er, 0.058 and 0.0215 for Tm and 0.00 and 0.0028 for Yb.

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Keywords: ferroelectricity, PLZT, rare earth

P.11.13.1*Acta Cryst.* (2005). **A61**, C400-C401**In-situ Study of Residual Strain in Solid Oxide Fuel Cells**René V. Martins^{a,b}, Anke Hagen^a, Veijo Honkimäki^c, Henning F. Poulsen^a, Robert Feidenhans'l^{a,d}, ^a*Risø National Laboratory, Roskilde, Denmark.* ^b*GKSS Research Centre Geesthacht, Germany.* ^c*European Synchrotron Radiation Facility, Grenoble, France.* ^d*Niels Bohr Institute, Copenhagen University, Denmark.* E-mail: rene.martins@gkss.de

Solid Oxide Fuel Cells (SOFC) are electrochemical devices converting the chemical energy of a fuel directly to electricity. Due to the high efficiency of the process they are considered as one of the most promising power production technologies of the future.

Among various designs of SOFCs, the so called flat cell design is subject to extensive research at the Risø National Laboratory and presently produced there in a pre-pilot cell production plant. The flat cell is a 3-layer structure consisting of a ~300 µm thick supporting anode layer of NiO-YSZ (Ytria Stabilized Zirconia, YSZ), a ~10 µm thick solid YSZ electrolyte, and a ~24 µm thick LSM-YSZ cathode (Strontium doped Lanthanum Manganite, LSM). The NiO in the anode is reduced to Ni under operating conditions.

In-situ diffraction experiments were performed on SOFC under standard operating conditions, more specifically during successive cycles of reduction and reoxidation at ~ 850 °C.

The experiment was performed with the spiral slit set-up at beamline ID15 at the ESRF and an X-ray wavelength of $\lambda = 0.173$ Å.

The strain distribution within the three constituent layers of the SOFC was determined from the distortion of the monitored Debye-Scherrer-rings.

Keywords: solid oxide fuel cell, residual stress measurement, in-situ observation

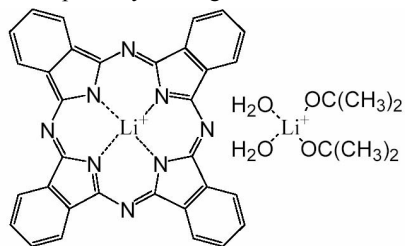
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A Crystallographic Examination of Dilithium Phthalocyanine

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Dilithium phthalocyanine is a compound that shows promise as the dielectric for lithium-lithium ion batteries. The compound forms small, flakey crystals from the few solvents in which it can be dissolved. Experimental evidence indicates that the lithium atoms within the solid structure migrate in the presence of an electric field. The determination of the crystal and molecular structure was initiated so as to determine the pathways through which the lithium ions move.



A=12.8017(6), b=14.3637(7), c=17.3859(8), α =101.5838(9), β =94.1351(9), γ =92.3054(9), V=3118.7(3), λ =0.71073Å, T=173K, R_{int}=0.0187, R₁=0.0484, wR₂=0.1351, S=1.046, Obs=18798, Par=1116.

Keywords: battery materials, crystal structure determination, lithium batteries

P.11.13.3

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Site Preference of Valence Ions in Fe_{1+x}Co_{2-x}O₄ (0 ≤ x ≤ 1)

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Iron cobaltites show the ferrimagnetism to have a spinel structure, where Co and Fe ions occupy tetrahedral A and octahedral B sites in various valence states. Therefore, the determination of cation distribution between the two kinds of sites is indispensable to the interpretation of the magnetic properties of cobaltites.

Fortunately, we succeeded to synthesize single crystals of Fe_{1+x}Co_{2-x}O₄ (x = 0.2) by the hydrothermal reaction. The site occupancy of Fe and Co ions was first determined by the single-crystal synchrotron X-ray diffraction method, where the anomalous scattering effect was used at the Co K absorption edge ($\lambda = 1.6182$ Å) in the BL-10A station of the Photon Factory. Then, the electronic information from X-ray absorption near edge structure (XANES) and X-ray magnetic circular dichroism (XMCD) spectra was utilized for determining the valence states of Fe and Co ions. The absorption experiments were performed at both Fe K and Co K edges at BL-3A. It was found that all Fe ions exist as trivalent ions in Fe K XANES spectra, while the valences of Co ions were uniquely obtained from the intensity variation of XMCD signals in the solid solutions [1].

Based on the full determination for x = 0.2 sample, the most plausible chemical formula and magnetic structures have been

suggested through the solid solution of Fe_{1+x}Co_{2-x}O₄ (0 ≤ x ≤ 1).

[1] Kita N., Shibuichi N., Sasaki S., *J. Synchrotron Rad.*, 2001, 8, 446.

Keywords: cation distribution, cobalt compounds, X-ray magnetic circular dichroism

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Structures of Defect Perovskites Suitable for Li Ion Intercalation

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The phase Sr₇Zr₄Nb₆O₃₀ in the SrO-ZrO₂-NbO_{2.5} system was recently discovered in our laboratories. X-ray diffraction patterns have shown that the compound Sr₇Zr₄Nb₆O₃₀ forms a cubic perovskite substructure with an additional modulation (satellite reflections at $\frac{1}{2}\langle 111 \rangle_p$). This compound is analogous to the perovskite Sr_xNbO₃, 0.7 ≤ x ≤ 1, which exists over a significant range of composition [1]. In contrast to our new phase Sr_xNbO₃, 0.7 ≤ x ≤ 1, does not display additional ordering (no satellite reflections were found despite intensive searching). Therefore it is likely that the additional reflections for our new phase are due to Nb/Zr ordering.

If x in the Sr_xNbO₃ solid solution equals 1 all the niobium is in oxidation state +IV. Reducing the amount of strontium leads to vacancies on that site and to a corresponding amount of Nb⁺⁵ required for charge balance. The vacancies on the Sr site allow Li to be intercalated electrochemically. In Sr₇Zr₄Nb₆O₃₀, all Nb⁴⁺ has been replaced by Zr⁴⁺, which allows syntheses to be carried out in air at high temperature. Preliminary investigations [2] have shown that a significant amount of Li can be intercalated, which would make that compound suitable as a cathode in a Li ion battery. The apparent reversibility of the intercalation process is another indication that this new phase might be suitable for that application.

[1] Hessen B., Sunshine S. A., Siegrist T., Jimenez R., *Mater. Res. Bull.*, 1991, 26, 85. [2] Schmid S., Kuhn A., unpublished.

Keywords: defect perovskite, lithium intercalation, lithium battery

P.11.14.1

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Residual Stress Distribution Near HA Coating Interface on Titanium Alloy Substrate

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Titanium alloys (Ti-6Al-4V) are largely used to realise fixed and mobile biomechanical prostheses, to be implanted for long times inside the human body, such as dental implants and hip prostheses. In order to prevent damage due to the relevant mechanical stresses and corrosive environment inside the human body, coatings are usually applied to provide a surface with properties such a good biocompatibility, corrosion protection, wear resistance, high strength and low cost. Hydroxyapatite (HA, Ca₁₀(PO₄)₆(OH)₂), as the major mineral component of bones and teeth, is used in implants as a coating, obtained by vacuum plasma spray deposition process. Although it has excellent bioactivity HA has poor intrinsic mechanical properties, so it is often coated on metallic substrates. This creates a device that combines good surface bioactivity with the strength of the metallic substrate.

A mechanical characterisation of the HA, coated on Ti-6Al-4V substrate is fundamental for the determination of the characteristics that the material provides from a functional point of view. Together the determination of microstructural features, it is very important to evaluate the residual stresses (RS) induced by deposition process, due to the different thermo-physical properties of the substrate and coating, as RS strongly influence the wear resistance of the coating. In this paper, X-ray diffraction stress in the ceramic coating and in Ti-6Al-4V substrate are presented and related to other experimentally determined microstructural parameters.

Keywords: TEM characterization, residual stress analysis, X-ray diffraction