

P.11.11.7*Acta Cryst.* (2005). A61, C397**Synthesis, Nuclear structure, and Magnetic Properties of Some Doped Perovskites**Roland Tellgren, Mehreteab Tseggai, Per Nordblad, *The Angstrom Laboratory, Uppsala University, Box 531, SE-751 21 Uppsala, Sweden.* E-mail: rte@mkem.uu.se

The compositions and purity of polycrystalline powder samples of $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Mg}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3$), $\text{LaCr}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3$) and $\text{La}_{1-x}\text{Nd}_x\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ ($x = 0.0, 0.15, 0.2$) were characterized by X-ray diffraction and chemical analysis. The magnetic properties were investigated by neutron powder diffraction technique and magnetization measurement using a SQUID.

All the structures studied have orthorhombic structure, space group Pnma, in a wide range of temperatures. The Mg-substitution in $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Mg}_x\text{O}_3$ creates only small distortions in the nuclear structure. The magnetic properties of the compounds, however, are significantly affected by Mg- substitution.

All the samples of nominal composition $\text{LaCr}_{1-x}\text{Mn}_x\text{O}_3$ have orthorhombic structure with space group Pnma at temperatures between 1.5 and 400 K. However, at 600 K, all samples are found to have rhombohedral structure with space group R-3c. The magnetic properties of the system are markedly affected by Mn-substitution. The parent compound, LaCrO_3 , is purely G-type antiferromagnetic with Neel temperature at about 300 K. With increasing Mn-substitution, gradually, a ferromagnetic component develops in the system, thereby leading to the occurrence of canted magnetic moment.

The magnetic structure of $\text{La}_{1-x}\text{Nd}_x\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ is antiferromagnetic, G-type, from room temperature down to 10 K. A small ferromagnetic component appears at the lowest temperatures.

Keywords: magnetic perovskites, antiferromagnetic, superexchange

P.11.11.8*Acta Cryst.* (2005). A61, C397**On the Initial Stage of Plastic Deformation of SrTiO_3** Peter Paufler, André Belger, Beate Bergk, Dirk C. Meyer, Alexander Levin, *Chair of Crystallography, Institute of Structural Physics, Dresden University of Technology, D-01062 Dresden, Germany.* E-mail: paufler@physik.tu-dresden.de

Nanoindentation experiments have been performed on {100}-, {110}- and {111}- oriented single crystals at room temperature. Force-displacement curves $F(h)$ showed pop-ins at $F > 500\mu\text{N}$. Their depth Δh varied between $\Delta h = 1 \dots 20$ (for {100} and {110}) or $= 5 \dots 40$ nm (for {111}). They indicate the onset of plastic deformation and correspond to extreme strain rates of 20s^{-1} . Connected with pop-ins, slip bands starting from the indent have been observed which are parallel to macroscopically active zones of slip planes {011} or {100}. They are also compatible with the slip direction $\langle 0-11 \rangle$ (cf. [1]). These bands propagate proportionally to both the depth of the indent and the contact pressure beneath the indenter. Extrapolating $\Delta h(\sigma) \rightarrow \Delta h = 0$ gives the following critical contact pressures p_c , when plastic deformation should set-in during increase of load. We found $p_c/\text{GPa} = 19.0$ (100), 20.0 (110), 23.00 (111) GPa for the three surface orientations (hkl), which are of the order of $E/10$. This stress level and the energy associated with a pop-in let us assume that spontaneous generation of dislocations occurs during a pop-in. Unlike macroscopic plastic deformation, which starts at a flow stress of 0.15 GPa [1], nanoindentation probes only part of the crystal $< d^3$ where no grown-in dislocations (average spacing d) will be encountered, hence stresses higher at 2 orders of magnitude are required.

[1] Brunner D., Taeri-Baghadrani S., Sigle W., Rühle M., *J. Am. Ceram. Soc.*, 2001, **84**, 1161

Keywords: nanohardness, plastic deformation, dislocations

P.11.11.9*Acta Cryst.* (2005). A61, C397**Nano-Structure of PLD-Grown Epitaxial $\text{PbTiO}_3/\text{BaTiO}_3$ Superlattices by Synchrotron X-ray Diffraction**Eric Dooryhée^a, Maud Nemoz^a, Jean-Louis Hodeau^a, Françoise Le Marrec^b, Nathalie Lemée^b, Michael Karkut^b, ^a*Lab. Cristallographie, CNRS, 25 av. des Martyrs, BP166, 38042 Grenoble, France.* ^b*Lab. de Physique de la Matière Condensée, 33 rue St-Leu, 80039 Amiens, France.* E-mail: eric.dooryhee@grenoble.cnrs.fr

By combining different ferroelectric layers, such as PbTiO_3 (PTO), BaTiO_3 (BTO) into artificially modulated structures, it is possible to investigate the role that size and interface play in the ferroelectric phase transition, the ferroelectric coupling across dielectric layers, the effects of strain on the ferroelectric properties. The physical behaviour of such compounds is primarily by their epitaxial crystalline quality, their composition and their structural perfection. We have extended a diffraction model⁽¹⁾, previously applied on metallic and semiconductor multilayers, to the more complex case of $(\text{PTO}/\text{BTO})_n$ perovskite superlattices. The entire (001) diffraction profiles of the $(\text{BaTiO}_3/\text{PbTiO}_3)_n$ superlattices are fitted over 8 orders of diffraction ($L=1$ to 8). We evaluate the coherence length, the interface roughness, the discrete thickness fluctuations, and the intra-layer gradients of strain and atomic diffusion in the $\langle 001 \rangle$ growth direction.

Probing the reciprocal space along $\langle 100 \rangle$ and $\langle 010 \rangle$ shows the distribution and orientations of coherent domains and their respective unit cell dimensions parallel to the growth plane. Our diffraction measurements support the presence of $\{a\}$ domains, i.e. the polar axis of PbTiO_3 is parallel to the surface, as a result of large lattice relaxation.

[1] Fullerton et al., *Phys. Rev.*, 1992, **B45**, 9292.

Keywords: multilayers, perovskite oxides, $\text{BaTiO}_3/\text{PbTiO}_3$

P.11.11.10*Acta Cryst.* (2005). A61, C397**Tolerance Factors and Solid Solutions in Three-Layer Aurivillius Ceramics**Scott T. Mixture, S.A. Speakman, E. Henriques, H-J Kim, *New York State College of Ceramics at Alfred University, 2 Pine St., Alfred, NY 14802, USA.* E-mail: mixture@alfred.edu

The Aurivillius phases are of interest in ferroelectric random access memory devices. We present first a range of solid solubility data for isovalent and aliovalent doping in the 3-layer Aurivillius phases that were prepared using solid state and polymerized complex methods. A range of approximately 100 compositions were investigated, and many were evaluated using electrical conductivity measurements to determine the total conductivity and type of charge carriers.

Early reports of tolerance factors, similar to those developed by Goldschmidt for perovskites, have been revisited by considering strain between the structural layers and the total oxygen concentration. Neutron diffraction results that include bond valence sum calculations show that the static disorder that is often observed in the Aurivillius phases in the form of site mixing between the large cation in the perovskite block and Bi in the $[\text{Bi}_2\text{O}_2]^{2+}$ layer. The interlayer strains evidenced from the calculations are supported by the experimental results. Finally, the model is used to show that the average oxidation state of cations that can take mixed valence, for example the transition metals, is a function of the strains imposed by the layered structure.

Keywords: Perovskite structures, structural stability, ferroelectrics

P.11.11.11*Acta Cryst.* (2005). A61, C397-C398**Tensor Properties of Engineered Domain Configurations in KNbO_3 Crystals**Jiří Fuksa, *Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic.* E-mail: fuksa@fzu.cz

Using a general method [1], [2], recently implemented in [3], we determine possible macroscopic types of engineered domain configurations of the $Amm2$ -phase in potassium niobate crystals. We find that among 17 types of the domain configurations that can be, theoret-

ically, produced by external fields there are 10 types of configurations with non-zero average polarization. It appears that electric field, possibly in combination with mechanical stress, may induce 7 non-equivalent coherent configurations formed each by equivalent domain states with same free energy in the field(s). The form of average tensor properties is given by the corresponding effective symmetry.

By examining tensor properties of the coherent configurations (CC's) we establish five cases where additional relationships between tensor components exist for certain material properties, compared to what is usually obtained for single domain crystals with same macroscopic symmetry. In one case even the stabilizer of each polar tensor of even rank differs from common expectations.

For representative CC's we specify average material tensors up to rank 4 in terms of tensor components of the same selected state.

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[1] Fuksa J., Janovec V., *J. Phys.: Condens. Matter*, 2002, **14**, 3795. [2] Fuksa J., Janovec V., *Ferroelectrics*, 2003, **292**, 37. [3] Fuksa J., Janovec V., 'Conceivable engineered configurations of monoclinic Cm-phases in relaxor PZN-PT crystals', *in press*.

Keywords: engineered domain configurations, effective symmetry, average tensor properties

P.11.12.1

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Lattice Parameters of the PZT 90/10 Ceramic doped with La

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The PZT ceramics have been attracting with considerable attention in a number of different context. One of them are their ferroelectrical properties.

Sample of $\text{Pb}_{0.94}\text{La}_{0.06}\text{Zr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ was prepared by sol-gel process and sintered at 1200°C for 2 hours.

Investigation lattice parameters of the specimen were studied using X-ray diffraction (XRD). X-ray traces were recorded using a Phillips diffractometer between 20°-110° (CuK α radiation) with scan step of 0.02° and scan time 14s/step.

In agreement with phase diagram for PLZT system [1] our sample should have a tetragonal structure. To confirm that assumption we prepared two simple simulated scans for tetragonal and rhombohedral structure. On the basis of the results and other data [2] we agreed with that assumption and made preliminary analysis of lattice parameters in profile matching mode. As a results of our investigation we obtained a following parameters: $a=b=4,1051\pm 0,0007\text{Å}$, $c=4,1194\pm 0,0005\text{Å}$.

[1] Hertling G.H., Land C.E., *J. Am. Ceram. Soc.*, 1971, **54**, 1. [2] Knudsen Jasper, Woodward D.I., Reaney I.M., *J. Mater. Res*, 2003, **18**, No.2.

Keywords: ferroelectrics, ceramic materials, powder X-ray diffraction

P.11.12.2

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Structural Phase Transitions and Hydrogen bonding in $\text{Rb}_3\text{H}(\text{SO}_4)_2$

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Compounds of the type $\text{A}_3\text{H}(\text{XO}_4)_2$, where $\text{A} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$, $(\text{NH}_4)^+$ and $\text{X} = \text{S}, \text{Se}$ are known ferroelectric and paraelectric materials. Recently, structural phase transition in $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ have been studied in detail [1]. We have investigated the phase transition in the analogous $\text{Rb}_3\text{H}(\text{SO}_4)_2$, the structure of which at room temperature was determined by Fortier *et al.*[2]. in 1985, at four different temperatures to follow the phase transition behavior. The data were collected on a Bruker Smart Apex CCD system equipped with an

Oxford cryostat at 293K, 100K, 393K and 425K respectively. The hydrogen atom is localized at the midpoint at 100K with respect to the sulfate tetrahedra while at room temperature it is connected with one of the oxygen atoms. DSC studies on a single crystal of the compound indicate phase transitions around 399K and 425K. The crystal structures of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ at four different temperatures show subtle conformational and packing changes and the geometry around the Rb atoms shows different coordination with respect to temperature.

[1] Dominiak P. M., Herold J., Kolodziejski W., Wozniak K., *Inorganic Chemistry*, 2003, **42**, 1590. [2] Fortier S., Fraser M.E., Heyding R.D., *Acta Cryst.*, 1985, **C41**, 1139.

Keywords: phase transition, hydrogen bonding, coordination

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Relaxor Ferroelectric Behaviour of $\text{Ba}_{1-x}\text{A}_x(\text{Ti}_{0.7}\text{Zr}_{0.3})\text{O}_3$ Compositions (A=Ca,Sr)

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The relaxor ferroelectric materials exhibit a large range of interesting properties related to their complex order/disorder nanostructures. The relaxor behaviour is well known in lead based compositions. Nevertheless, the latter present a disadvantage due to the toxicity of polluting substances. The actual evolution of research is directed to replace the lead by lead-free compositions [1, 2]. The aim of the present work was to prepare and to characterize some ceramics derived from BaTiO_3 by cationic substitution in the 12-C.N crystallographic site.

The various compositions were obtained by solid state synthesis. Room temperature X-ray diffraction analysis allowed us to determine the limits of solid solution. Dielectric measurements exhibit a relaxor behaviour in the range $0 < x < 0.20$. Whatever A, T_m decreases as x increases. However, the decrease was comparatively lower in the case of the calcium substitution. This result is related to the size of each cation. For the Ba-Sr substitution the decrease of T_m results from reduction of the c/a ratio. On the contrary, for the Ba-Ca substitution, Ca^{2+} induces a local polar moment leading to a small decrease of T_m . Concerning the strontium substitution, one of the noteworthy characteristic is the very high value in the maximum of ϵ'' .

[1] Ravez J., Simon A., *J. Korean Phys. Soc.*, 1998, **32**, 955. [2] Nagata H., Takeda T., *Spn. S. Appl. Phys.*, 1998, **37**, 5311

Keywords: ferroelectric relaxors , lead free materials , disordered materials

P.11.12.4

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Ferroelectric Phase Transition Mechanism in $\text{C}_5\text{H}_6\text{NBF}_4$ by X-ray Crystal Analysis

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Pyridinium Tetrafluoroborate $\text{C}_5\text{H}_6\text{NBF}_4$ (abbreviated to PyBF_4) undergoes a ferroelectric-paraelectric phase transition at $T_1=238.7\text{K}$, and another phase transition at $T_2=204\text{K}$ [1, 3]. From the NMR studies [2], the pyridinium and tetrafluoroborate ions were the dynamical disorder state at room temperature. It was suggested that the ordering of these ions was linked to the successive phase transitions. From the X-ray diffraction study [3], the disorder state of the pyridinium and tetrafluoroborate ions was also reported. However, a report of the crystal structure analysis at low temperature was not found. The crystal structure analyses at low temperature phases in PyBF_4 were very important in order to clarify the mechanism of the successive phase transition in this material.

Re-investigation of the single-crystal X-ray structure analysis in