

polycrystalline fcc, bcc and hcp metals and alloys. Plastic flow regularities are found to occur from yield limit to failure as macro-localization patterns.

It is found that active localized plasticity nuclei would emerge and evolve on the macro-scale level over the entire flow process. These nuclei can be regarded as meso-scale defects responsible for plastic flow development on the macro-scale level. Their salient feature is that the spatial distributions of elongation, shear and rotation increments within a nucleus are interrelated. Each active localization nucleus corresponds with a set of shears or deformation twins over the glide plane of the acting glide or twinning system, which have maximal Schmidt factor values. A space-time localization pattern results from dislocation self-organization; this has wave features, i.e. length  $5 < \lambda < 10$  mm and rate  $10^{-5} < V < 10^{-4}$  m/s. A two-component model of plastic flow self-organization is proposed, which is based on the interaction of the crystal's phonon and dislocation sub-systems. This reconciles commonly known dislocation mechanisms acting at the various deformation hardening stages in single crystals and accounts for the above regularities of wave generation. The basic assumptions of the model are as follows. Relaxation-type plasticity involves dislocation acts that generate acoustic emission pulses causing elastic energy re-distribution among the stress concentrators (dislocations). As a result, the stresses at the concentrators grow to initiate their relaxation by dislocation shears. The sequence of events is repeated. For relaxation events to be activated, stress concentrators of the same type and size must be initiated, which is provided by acoustic pulses of strictly specified shape and spectrum, their amplitude being less significant. The concepts of defect self-organization and of energy re-distribution among stress concentrators involved successively in relaxation acts, might help account for the low values of localization wave rate and for the large-scale correlations of localization domains occurring in a deforming system that only contains micro-scale defects (dislocations). Thus, use of the above model allows one to explain the most important features of plastic deformation localization and transition to necking and failure in solids.

[1] Zuev L.B., *Ann. Phys.* **2007**, 16, 286.

**Keywords:** plasticity; wavelength; localisation

#### FA3-MS04-P06

##### Reversible Structural Changes by Electrostatic Fields in Strontium Titanate at Room Temperature.

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While strontium titanate (SrTiO<sub>3</sub>) is mainly used as substrate material, its high dielectric permittivity makes it an interesting material for electronic and other applications. Its

properties strongly depend on the defects in its perovskite-type of structure, even at room temperature. Mobile oxygen can cause the formation of non-stoichiometric regions when an electric field of sufficient strength (~1000 V/mm) is applied. Our *in-situ* investigations revealed reversible structural changes at room temperature caused by a systematic field-induced redistribution of oxygen.

The structural changes are highlighted by means of wide-angle X-ray scattering, X-ray absorption spectroscopy, nanoindentation and time-resolved measurements of the electric current. We found a reversible conversion of the perovskite structure to a long-range ordered variant with changed lattice parameter. The temporal change of the structure of SrTiO<sub>3</sub> at near-surface regions (depth in the order of 10 μm) can be described by a model assuming solid-state electrolysis at room temperature driven by the electric field applied. Local changes of the refraction index caused by stress birefringence were discovered by optical polarization microscopy. These local stress fields may be attributed to dislocation cores acting as paths for the oxygen transport to the anode. From spectroscopic measurements showing a change of titanium valence in near-surface regions, we can prove the oxygen diffusion model. Effects on the mechanical properties, i. e. hardness and elasticity were measured and compared to ab-initio simulations. Our results reveal the possibility of structurally modifying the technologically relevant perovskite oxides using electrostatic fields. The tunable lattice spacings observed might be used in the field of adaptive X-ray optics. Also, substrates with tunable dielectric properties at constant basal lattice parameters could be realized.

**Keywords:** crystals in electric fields; solid-state structural changes; structure-properties relationships

#### FA3-MS04-P07

##### Temperature-dependent X-ray Diffraction Studies of Mullite-type (Bi<sub>1-x</sub>Sr<sub>x</sub>)<sub>2</sub>M<sub>4</sub>O<sub>9</sub> Phases. Reinhard X. Fischer<sup>a</sup>, Hartmut Schneider<sup>a</sup>, Thorsten M. Gesing<sup>a,b</sup>.

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The temperature-dependent behavior of Bi<sub>2</sub>M<sub>4</sub>O<sub>9</sub> compounds, known to have potential as electrolytes in solid oxide fuel cells (SOFC) [1], was investigated by X-ray powder diffraction methods using a Paar HTK 1200N heating chamber. Data were recorded at 298 K and between 323 K and 1273 K in steps of 50 K in heating and cooling cycles. Three compositions were used for these investigations: Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, Bi<sub>2</sub>Al<sub>4</sub>O<sub>9</sub> and (Bi<sub>0.8</sub>Sr<sub>0.2</sub>)<sub>2</sub>Al<sub>4</sub>O<sub>9</sub> were synthesized using the glycerin method as described in [2] and finely ground in acetone.

For Bi<sub>2</sub>Al<sub>4</sub>O<sub>9</sub>, a similar heating and cooling behavior of the metric parameters was observed showing thermal expansions of  $5.5 \cdot 10^{-6}$ ,  $9.4 \cdot 10^{-6}$ ,  $7.8 \cdot 10^{-6}$  and  $2.3 \cdot 10^{-5}$  for the lattice parameters *a*, *b*, *c*, and for the unit cell volume *V*, respectively. No phase transitions or unexpected structural changes are observed. From TG/DTA measurements the phase stability up to 1429 K can be derived. For the

tetrahedrally and octahedrally coordinated aluminum atoms the same relative displacement (percentage movement in relation to the ionic radii) is observed which is twice as high as compared with the values calculated for the bismuth and oxygen atoms.

For  $(\text{Bi}_{0.8}\text{Sr}_{0.2})_2\text{Al}_4\text{O}_9$ , the thermal expansion parameter of  $5.3 \cdot 10^{-6}$ ,  $9.6 \cdot 10^{-6}$ ,  $6.7 \cdot 10^{-6}$  and  $2.3 \cdot 10^{-5}$  for the lattice parameters  $a$ ,  $b$ ,  $c$ , and  $V$ , respectively, measured during heating runs of two different samples, differ slightly from the corresponding parameters of the pure bismuth aluminate. Additionally, during the cooling run the thermal expansion for the  $c$  lattice parameter ( $7.9 \cdot 10^{-6}$ ) differs at most from the heating measurement. But in both cases, the samples were heated above their stability temperature of 1070 – 1130 K and this parameter reflects the remaining  $(\text{Bi}/\text{Sr})_2\text{Al}_4\text{O}_9$  phase to be nearly free of strontium which is confirmed by Rietveld refinements.

For  $\text{Bi}_2\text{Fe}_4\text{O}_9$ , a similar behavior as for the corresponding aluminate or gallate [3] is observed except the decomposition temperature, which is 1232 K for the ferrate.

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- [1] Goodenough, J.B.: *Ann. Rev. Mater. Res.* 33, **2003** 91-128. [2] Gesing Th. M.: *Z. Kristallogr. Suppl.* 29, **2009** 92-93., Hannover. [3] Gesing, Th.M., Schneider H., Fischer R.X. Burianek, M., Mühlberg, M.: *Z. Kristallogr. Suppl.* 29, **2009** 84-85.

**Keywords:** mullite related phases; high temperature; powder diffraction

#### FA3-MS04-P08

**Synthesis and Crystal Structure of  $\text{Zr}_{0.43}\text{Gd}_{0.57}\text{O}_{1.07}\text{N}_{0.43}$ .** Eberhard Schweda<sup>a</sup>, Stefanie Meyer<sup>a</sup>. <sup>a</sup>Universität Tübingen, Institut für Anorganische Chemie, Ob dem Himmelreich 7 D-72074 Tübingen.

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The nitridation of  $\text{Zr}_{0.43}\text{Gd}_{0.57}\text{O}_{1.71}$  using gaseous ammonia leads to a solid solution type nitride oxide with the composition  $\text{Zr}_{0.43}\text{Gd}_{0.57}\text{O}_{1.07}\text{N}_{0.43}$ . The reaction path was recorded using in situ X-ray diffraction. The nitridation introduces additional vacancies into the fluorite lattice and the composition of the title compound counts for an  $\text{M}_2\text{X}_3$  structure type if there is any ordering of vacancies. Unlike  $\text{Zr}_{0.43}\text{Er}_{0.57}\text{O}_{1.07}\text{N}_{0.43}$ , which crystallizes in Ia3 with a bixbyite type structure and ordered vacancies [1], the Gd compound has a complete statistical distribution and crystallizes in space group Fm3m with lattice constant  $a = 527.2(2)$  pm

- [1] Meyer S., Schweda E., 17 Jahrestagung DGK Hannover, **2009** A40, 29.

**Keywords:** zirconium nitride oxide

#### FA3-MS04-P09

**Crystallization and Microstructure Evolution of TiO<sub>2</sub> Thin Films and Powders Studied by XRD Total Pattern Fitting and Stress Analysis.** Radomir Kužel<sup>a</sup>, Zdenek Matěj<sup>a</sup>, Lea Nichtová<sup>a</sup>. <sup>a</sup>Department

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Different TiO<sub>2</sub> samples – magnetron deposited amorphous and nanocrystalline thin films and powders – were annealed both off-situ and in-situ in XRD high-temperature chamber and their microstructure evolution with temperature and time was studied.

Coplanar XRD grazing incidence measurements (2θ scans) in parallel beam setup with a mirror were evaluated by both the profile fitting of peak clusters and total pattern fitting. Residual stresses were analyzed by sin<sup>2</sup>ψ method and X-ray reflectivity curves were studied as well. Because of severe peak overlap the whole pattern evaluation was applied in most cases. We have extended flexible modular system of Crystal Objects and Fox program [1] for studies of real structure of thin films. Applied model include the following features. Variable peak positions determined by variable lattice parameters and zero shift error, possibly also by residual stress. Peak intensities calculated by the ObjCryst library from a known crystal structure model. They can be modified by absorption and the texture correction obtained from the known model of ODF after numerical integration over all crystallites with diffracting (hkl) planes perpendicular to direction of the measured diffraction vector, or they can be varied independently. Peak profiles are given by numerical convolution of the known instrumental function described by the pseudo-Voigt function and physical profiles including several free parameters (models). The size broadening is described by the model of log-normal distribution of spherical crystallites or distribution given by a histogram like in [2], the strain broadening either by phenomenological microstrain or dislocation model. Stacking faults and twins can be included too. Individual layers in the system are characterized by their thickness and linear absorption coefficient.

It was shown that crystallization of very thin *amorphous* films (below about 300 nm) is rather slow. Fast crystallization occurred in the temperature range 220–300°C depending on the films thickness. In this case relatively large crystallites (> 100 nm) grew quickly from the very beginning of crystallization and they were not changed with increasing annealing time. The microstructure evolution was different for powders when the crystallites grew with annealing time to some saturated values determined by the annealing temperature. By contrast as-deposited *nanocrystalline* films (crystallite size ~ 5 nm) or nanocrystalline powders showed the fine microstructure stable to quite high temperatures (500 °C) before the strain relaxation and crystallite growth was observed.

During the crystallization of amorphous films tensile residual stresses were generated. They were of simple uniaxial character and strongly increase with decreasing film thickness.

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**Keywords:** titanium dioxide; total pattern fitting; microstructure