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Synthesis, Structure and Thermal Behaviour of a Strontium-Pimelate Framework. Khadidja Aliouane^a, Achoura Guehria-Laidoudi^a, Slimane Dahaoui^b, Claude Lecomte^b. ^a*Laboratoire de Cristallographie-Thermodynamique, Faculté de Chimie, USTHB, BP 32 El-alia, Bab Ezzouar 16111, Alger.* ^b*CRM²-UPRESA 7036, Université Henri Poincaré BP 239, 54506 Vandoeuvre-lès-Nancy, France.*

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New generations of metal-organic coordination polymers have emerged in last years, enhancing the field of supramolecular chemistry. These compounds, based on building unit concept, are constructed from connectors assuming a great coordination number and linkers offering versatile coordination modes. With this purpose, and extending our previous work, we present the synthesis, structure and thermal behaviour of a non-templated strontium pimelate consisting of isolated SrO₈ polyhedra bridged in layers.

Single crystals were obtained by soft chemical process. At the pH value adjusted in the gel diffusion technique, pimelic acid deprotonates partially, bringing out the supramolecular bonding feature [HO₂C-(CH₂)₅-CO₂]⁻. The hybrid polymeric structure, belonging to space group P4₂/m^b exhibits inorganic layers parallel to (001). Organic chains formed by the carbon backbone of the ligands run roughly along c axis. In the extended network, two end carboxylic groups are in anti-parallel orientations. The two-dimensional substructure containing Sr atoms forms a pseudo-eight-sided grid network with empty channels. There is no M-O-M infinite linkage which is the typical feature appearing in the most polycarboxylate complexes and particularly in lanthanum [1] and cerium [2] pimelates. This new compound is structurally closely related to the barium-glutarate previously studied [3], presenting the same space group and architecture. It seems that c parameter is modified according to the longest spacer (7 C atoms instead of 5). The thermal studies indicate a high stability if compared to other earth-alkaline polymers. However, unlike the lanthanum and the cerium pimelates which can be affiliated to the third generation of coordination polymers [4], the total weight loss doesn't exceed the calculated one corresponding to SrCO₃ as residue. The a and c unit cell parameters evolution, studied over the temperature range (100-293)K shows a monotonic variation. The crystal structure, investigated at room temperature, is completely different.

[1] B Benmerad, Doctorat, USTHB, Algiers, **2007**. [2] N Rahahlia, Doctorat, USTHB, Algiers, **2007**. [3] K. Aliouane, A. Djeghri, A. Guehria-Laidoudi, S. Dahaoui, C. Lecomte, *J. of Mol. Struct.*, **832**, 150, **2007**. [4] S Kitagawa, M Kondo, *Bull. Chem. Soc. Japan*, **71**, 1739, **1998**.

Keywords: pimelate; extended framework; coordination polymer

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The Crystal Structures of Polymorphs of Strontium Ranelate. Kenny Stahl^a, Christian G. Hartmann^a, Carsten B. Prag^a, Søren R. Sørensen^a, Anders C. Raffalt^a, Stephan Christgau^a, Jens E.T. Andersen^a. ^a*Chemistry Department, Technical University of Denmark, Lyngby, Denmark.*

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Recent preclinical and clinical investigations have revealed that Sr²⁺ reduces bone re-sorption while at the same time it provides a stimulation of new bone formation (Marie et al., 2001). This combined action on bone metabolism sets Sr²⁺ unique as compared to existing osteoporosis therapies and has led to a growing interest in Sr²⁺ salts with different organic anions. Several organic strontium salts has recently been synthesized and structurally characterized by single-crystal methods [2,3,4,5]. Strontium ranelate (5-[bis(carboxymethyl) amino]-3-carboxymethyl- 4-cyano-2-thiophenecarboxylate), is one promising pharmaceutical compound for treating osteoporosis marketed as Protelos[®] by Servier[®] [6]. The crystal structures of strontium ranelate nonahydrate and heptahydrate has now been determined by single-crystal diffraction (P-1, a=8.3585(5), b=12.6474(8), c=12.3865(8) Å, α=109.880(1), β=105.321(1), γ=97.148(1)° and P-1, a=8.3047(9), b=11.528(1), c=12.431(1) Å, α=112.939, β=101.971, γ=90.220(2)°, respectively). In situ variable temperature powder diffraction confirms the reversible transformation between the nona- and heptahydrates and a third phase was identified at 382 K (P-1, a=8.2372(4), b=11.3904(5), c=11.3978(9) Å, α=117.613(3), β=92.097(3), γ=94.297(3)°). The structures are built from edge-sharing of seven-, eight- and nine-coordinated Sr-polyhedra forming hollow layers perpendicular to (0-11) connected by ranelate ions. The water is partly coordinated to strontium and partly in the channels formed along the a-axis. The zeolitic nature of the latter water explains the easy transformations between the different forms of strontium ranelate.

[1] Marie et al., **2001**, *Calcif. Tissue Int.* **69**, 121-129. [2] Christgau et al. **2005**, *Acta Cryst. C61*, m259-m262. [3] Stahl et al. **2006**, *Acta Cryst. C62*, m144-m149. [4] Stahl et al. **2006**, *Acta Cryst. E62*, m1677-m1679. [5] Christgau et al. **2006**, *J. Coord. Chem.* **59**, 2023-2030. [6] Damien, **2006**. Patent No. 11/140,822. USA.

Keywords: strontium ranelate; polymorphism; dehydration

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Deformation Defects in Solids: from Dislocations to Plasticity Localization Waves. Lev Zuev^a, Svetlana Barannikova^a. ^a*Institute of Strength Physics and Materials Science, Tomsk, Russia.*

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Conventional dislocation approaches used by addressing plastic flow are re-considered in the light of a new wave concept of deformation macro-localization [1]. Holographic investigations were performed for single- and

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

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

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While strontium titanate (SrTiO₃) 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 SrTiO₃ 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

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Temperature-dependent X-ray Diffraction Studies of Mullite-type (Bi_{1-x}Sr_x)₂M₄O₉ Phases. Reinhard X. Fischer^a, Hartmut Schneider^a, Thorsten M. Gesing^{a,b}.

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The temperature-dependent behavior of Bi₂M₄O₉ 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: Bi₂Fe₄O₉, Bi₂Al₄O₉ and (Bi_{0.8}Sr_{0.2})₂Al₄O₉ were synthesized using the glycerin method as described in [2] and finely ground in acetone.

For Bi₂Al₄O₉, 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