

P.11.10.9*Acta Cryst.* (2005). **A61**, C395**Electron Density in Ga doped RTP**Joachim C. M. Gustafsson, Göran Svensson, *Chemical and Biological Engineering, Inorganic Chemistry, Chalmers University of technology Göteborg, Sweden*. E-mail: jogu@chalmers.se

Rubidium titanyl phosphates, RbTiOPO₄ (RTP) and isostructural compounds are well known for their non-linear optical properties. The properties may be varied by inclusion and/or replacement of rubidium, titanium and phosphorous by other elements. Some other characteristics like high optical damage thresholds and wide transparency windows are also beneficial for choosing these materials in optical applications.

Crystals were grown from a self-flux which was modified with addition of Ga₂O₃. Single crystals of good quality were obtained and the sizes range from a few microns up to approx 3 mm.

The crystals were structurally investigated using X-ray diffraction and neutron diffraction. The chemical composition was determined from SEM-EDX and measurements with SIMS were made for depth profile analysis of the crystals.

Keywords: electron-density, nonlinear materials, ferroelectric material

P.11.10.10*Acta Cryst.* (2005). **A61**, C395**Structural Changes of Sol-Gel derived Sn-doped In₂O₃ due to Annealing at 1000 °C**Biserka Grzeta^a, Emilija Tkalec^b, Christian Goebbert^c, Jasminka Popovic^a, Vadim Ksenofontov^d, Sergey Reiman^d, Claudia Felser^d, ^aRudjer Boskovic Institute, P.O. Box 180, HR-10002, Zagreb. ^bFaculty of Chemical Engineering and Technology, University of Zagreb, Marulicev trg 20, HR-10000 Zagreb, Croatia. ^cITN Nanovation, D-38820 Halberstadt. ^dJohannes Gutenberg-Universität, Staudinger Weg 9, D-55099 Mainz, Germany. E-mail: grzeta@irb.hr

Sn doped In₂O₃ (ITO) is an n-type, highly degenerate, wide-gap semiconductor. Its electrical and optical properties are associated with microstructure as well as with the preparation methods and conditions [1]. Although it is widely used in optoelectronic devices, its structure is not well understood yet. A set of ITO samples containing 0-14 at% Sn was prepared by a sol-gel technique from InCl₃ and SnCl₄ [2]. The samples were additionally annealed at 1000 °C for 1 h, slowly cooled to RT and examined by XRD and ¹¹⁹Sn Moessbauer spectroscopy. XRD revealed that the samples were isostructural with In₂O₃ [3]. Lattice parameter *a* increased almost linearly with Sn-content from the value of 10.1215(5) Å for pure In₂O₃ to 10.1319(4) Å for 14 at% Sn. While ¹¹⁹Sn Moessbauer spectra of the as-prepared samples are characterized with two doublets corresponding to two different cation sites (B and D, respectively), the spectra of annealed samples contained extremely broad subspectrum in addition. Decrease of temperature from 300K to 10K caused disappearance of the broad component. This unusual broad Moessbauer subspectrum could be explained by a diffusional motion of Sn⁴⁺ ions.

[1] Shigesato Y., Paine D. C., *Thin Solid Films*, 1994, **238**, 44. [2] Tkalec E., et al., *XX Congress IUCr*, 2005. [3] Marezio M., *Acta Cryst.*, 1966, **20**, 723.

Keywords: Sn-doped In₂O₃, X-ray diffraction, Moessbauer spectroscopy

P.11.10.11*Acta Cryst.* (2005). **A61**, C395**Push-Pull Mixed-Ligand d⁸-Metal Dithiolene Complexes**Luca Pilia^a, Paola Deplano^a, Cristophe Faulmann^b, Andrea Ienco^c, Carlo Mealli^c, Maria Laura Mercuri^a, Angela Serpe^a, ^aDCLA, Università di Cagliari, Italy. ^bLCC-CNRS, Toulouse, France. ^cICCOM-CNR, Florence, Italy. E-mail: pilialuc@unica.it

Recently an experimental and theoretical study on neutral, square-planar mixed-ligands nickel-bisdithiolenes has been performed [1]. These complexes have a common (C₂S₂)Ni(C₂S₂) core and two different terminal groups (R₂pipdt=1,4-dialkyl-piperazine-3,2-dithione; R₂timdt=1,3-dialkyl-imidazolidine-2,4,5-trithione as push ligands and dmit=1,3-dithio-2-thione-4,5-dithiolato; mnt=

maleonitriledithiolato as pull ligands). Measurements of the first molecular hyperpolarizability (β) indicated that some of the species are NLO chromophores, due the π -delocalized character of two frontier levels which is asymmetrically perturbed by the combination of one *push* with one *pull* ligand. Experimental results indicate rather different responses between the pairs of complexes containing R₂pipdt and R₂timdt ligands. DFT calculations have been carried out to correlate geometries and electronic structures. β values have been calculated and their components have been analyzed with the simplest two-level approximation. The derived picture highlights the different roles of the two *push* and *pull* ligands, but also the peculiar perturbation of the π -electron density induced by dmit. The novel complex [Pd(Me₂pipdt)(dmit)] has been obtained and shows negative solvatochromism. Its structural and electronic properties will be compared with those of the nickel analogue.

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Keywords: metal complexes, NLO, DFT

P.11.11.1*Acta Cryst.* (2005). **A61**, C395**Structures of Perovskite-related layered A_nB_nO_{3n+2}**Jonathan Guevarra^a, Sander van Smaalen^a, Nicola Rotiroti^a, Frank Lichtenberg^b, ^aLaboratory of Crystallography, University of Bayreuth, 95440 Bayreuth, Germany. ^bInstitut für Physik, EKM, Experimentalphysik VI, Universität Augsburg, Universitätsstraße 1, 86135 Augsburg, Germany. E-mail: jonathan.guevarra@uni-bayreuth.de

Perovskite-related oxidic compounds A_nB_nO_{3n+2} (where A = Ca, La or Sr and B = Ti or Nb) with n = 4, 4.5, 5, 6, and 7 have been the subject of much research, because of their one-dimensional metallic behavior which has been attributed to Peierls transition and charge-density wave [1,2]. Their structures are derived from the ABO₃ perovskite-type structure with additional layers of oxygen separating the slabs of BO₆ octahedra which are parallel to the (110) planes. The width of the slab is determined by the oxygen content and is given directly by the parameter *n*. In this study, single crystals of several of these compounds were prepared by floating-zone melting [1] and their crystal structures were determined at ambient conditions by single-crystal X-ray diffraction with synchrotron radiation using a CCD area detector. For some of these compounds superstructures were observed while some could be described by modulated structures. Particular attention is given to the distortions of the BO₆ octahedra and their variations across the width of the slabs, the different environments of the A cations, and the chemical ordering of these cations.

[1] Lichtenberg F., Herrnberger A., Wiedenmann K., Mannhart J., *Prog. Sol. State Chem.*, 2001, **29**, 1-70. [2] Kuntscher C. A., Schuppler S., Haas P., Gorshunov B., Dressel M., Grioni M., Lichtenberg F., Herrnberger A., Mayr F., Mannhart J., *Phys. Rev. Lett.*, 2002, **89**, 236403.

Keywords: X-ray diffraction, perovskite, A_nB_nO_{3n+2}

P.11.11.2*Acta Cryst.* (2005). **A61**, C395-C396**Structural Phase Transition of La_{0.815}Ba_{0.185}MnO₃ studied by X-ray Diffraction and the Maximum Entropy Method**Nicola Rotiroti^a, Rafael Tamazyan^b, Sander van Smaalen^a, Ya. Mukovskii^c, ^aLaboratory of Crystallography, University of Bayreuth, Bayreuth, Germany. ^bMolecule Structure Research Centre, Yerevan, Republic of Armenia. ^cMoscow State Steel and Alloys Institute, Moscow, Russian Federation. E-mail: nicola.rotiroti@uni-bayreuth.de

La_{0.815}Ba_{0.185}MnO₃ (rhombohedral, spacegroup R-3c) has been studied as one of the compounds in which the colossal magnetoresistance (CMR) effect occurs. Physical properties are often found to be strongly related to the structures of CMR compounds. For La_{0.815}Ba_{0.185}MnO₃ a metal-insulator transition and CMR take place at T_c=251K [1,2]. A first-order structural phase transition takes place at T_s≈196K. At the latter temperature, anomalies in both resistivity and magnetization temperature dependency have been observed. We

present the results of accurate structure determinations at several temperatures between 160 and 293K by single-crystal x-ray diffraction, in order to characterize the low temperature phase. To further clarify the structural changes as a function of temperature we have analyzed the diffraction data by the Maximum Entropy Method (MEM) [3] in a small temperature range close to the phase transition.

[1] Arkhipov V.E., et al., *Phys. Rev. B*, 2000, **61**, 11229. [2] Mukovskii Ya., et al., *J. Alloys and Compounds*, 2001, **326**, 108-111. [3] Smaalen S.V., Palatinus L., Schneider M., *Acta Cryst. A*, 2003, **59**, 459-469.

Keywords: manganites, CMR, MEM

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Comparison of $\text{Ba}_{0.05}\text{Sr}_{0.95}\text{RuO}_3$ and $\text{Ca}_{0.05}\text{Sr}_{0.95}\text{RuO}_3$ Structures

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SrRuO_3 , which has a nearly ideal perovskite structure, is a rare example of a 4d transition metal oxide that is metallic and ferromagnetic [1]. Its saturation moment is smaller than expected and it is usually considered an example of an itinerant ferromagnetism, however the nature of magnetism is not yet fully understood [2]. In spite of the structure of perovskite SrRuO_3 is described in the literature as orthorhombic, we have found this compound possesses a space group $\text{P}112_1/\text{m}$. This space group may be the clue to understand the low temperature magnetic behaviour.

In this work we have studied both solid solution $\text{Ba}_{0.05}\text{Sr}_{0.95}\text{RuO}_3$ and $\text{Ca}_{0.05}\text{Sr}_{0.95}\text{RuO}_3$ by powder X-ray diffraction at room temperature and at higher temperatures. In both compounds, weak observed reflections were not well refined in orthorhombic space group, like in pure SrRuO_3 . In the monoclinic structure, bond distances, angles and a bond valence sum study shows that, when cation Sr is replaced by Ba it is over-bonded, contrasting to the replacement by Ca. In order to diminish this valence sum, RuO_6 rigid groups tilt along the three cubic axes (in the Pnma space group, this is not possible with different angles). In order to detect the phase transition $\text{P}112_1/\text{m} \rightarrow \text{Pnma}$, a reexamination of the sequence of high-temperature phases in both compounds has been performed.

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Keywords: powder X-ray diffraction, perovskites, ferromagnetics

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Verwey Transition in a Perovskite-Type Structure

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Above Verwey transition at 120 K, magnetite (Fe_3O_4) is a spin-polarized conductor, feasible for applications in spin computing. Owing to continuing controversy about charge order in the complex low-temperature phase, Verwey transition in magnetite remains a mystery. Double-cell perovskites of the YBaFe_2O_5 type contain iron in the average oxidation state +2.5 and exhibit all symptoms of the Verwey transition. The charge-ordered superstructures are simple and the refined iron–oxygen bond distances suggest a 70 to 80% of long-range charge separation into di- and trivalent iron, likely to mean a 100% charge separation on the local scale. The charge order violates Coulombic minimization of point charges, implying orbital ordering. The associated orthorhombic distortion identifies the doubly-occupied d_{xz} orbital of Fe^{2+} . Magnetic interactions define the orientation of the orthorhombic distortion, but the charge order occurs independently of any specific spin coupling. Magnetostriction opens for an incipient partial charge ordering that occurs before the Verwey transition itself distorts the structure under continued cooling. Replacing Y with Sm and Nd shows that when the size of this seemingly uninvolved atom becomes unfavorable (a large projected ΔV at the transition), orbital ordering continues at a cost of symmetry lowering. Oxygen nonstoichiometry decreases Verwey-transition entropies ΔS and

transition temperatures T_V in a manner that corresponds to an ideal solution of YBaFe_2O_6 in the YBaFe_2O_5 solvent. Verwey transition is a klassengleich switch from a valence-mixed halfmetal into a valence-ordered semiconductor, achieved via orbital ordering of one single, singly or doubly occupied d orbital of t_{2g} symmetry.

Keywords: mixed valence oxides, phase transition, superstructure

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Nanostructural Effects at KNbO_3 Synthesis

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It was recently established that ferroelectric properties of oxides with perovskite-type structures (for example, BaTiO_3 and PbTiO_3) in nanocrystalline states were reduced [1,2]. The nature of ferroelectricity at nanoscale, such as critical size dependent suppression in particles, is much debated in the literature.

Attempts to understand further the finite size effect in ferroelectric oxides led us to studies of KNbO_3 synthesis process from K_2CO_3 and Nb_2O_5 stoichiometric mixture at different temperatures using X-ray diffractometer.

Special attention is paid to changes in symmetry, lattice parameters and dimensions of coherent scattering areas in synthesis and stabilization processes of KNbO_3 perovskite structure. It is found that there are correlations between microscopic (atomic parameters and lattice constants) and mesoscopic (dimensions of coherent scattering areas) characteristics of KNbO_3 structure which provide an opportunity to describe not only nanostructural effects but some physical parameters of KNbO_3 in dependence from nano-sizes of crystal phases.

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Keywords: perovskites, synthesis, nano-size effects

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Crystal Structure of the Layered Compound $\text{Sr}_3\text{NdFe}_3\text{O}_9$

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This compound belongs to the series $\text{Sr}_3\text{LnFe}_3\text{O}_9$ ($\text{Ln} = \text{La} - \text{Sm}$). An original feature of the latter ones is the rapid reaction with ambient moisture to transform into hydrated oxyhydroxide $\text{Sr}_3\text{LnFe}_3\text{O}_8(\text{OH})_2 \cdot \text{H}_2\text{O}$. [1] Previous electron microscopy and X-ray diffraction studies of $\text{Sr}_3\text{NdFe}_3\text{O}_9$, [1] revealed an orthorhombic lattice with parameters $a_p\sqrt{2} \times a_p\sqrt{2} \times 28 \text{ \AA}$ (a_p : lattice parameter of the perovskite). In a first time, the structure was considered as an oxygen deficient $n = 3$ R_p-Member $\text{Sr}_3\text{NdFe}_3\text{O}_9$. Powder neutron diffraction experiments at RT and 673 K were then carried out and show that the structure can be described as a stacking of blocks formed by two external slabs of FeO_6 octahedra and a central slab of FeO_4 tetrahedral. To this point of view this structure result of the intergrowth of Brownmillerite type blocks $\text{Sr}_{3/2}\text{Nd}_{1/2}\text{Fe}_2\text{O}_5$ with K_2NiF_4 type blocks $\text{Sr}_{3/2}\text{Nd}_{1/2}\text{FeO}_4$ instead of triple perovskite type blocks with adjacent NaCl type layers of SrO.

Powder Neutron diffraction data at Room temperature and susceptibility measurement although shows that this compound although present an antiferromagnetic transition at ~500 K

[1] Pelloquin D., Hadermann J., Giot M., Caignaert V., Michel C., Hervieu M. and Raveau B., *Chem. Mater.*, 2004, **16**, 1715.

Keywords: powder structure resolution, layered compound, magnetic properties