

**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, RbTiOPO<sub>4</sub> (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 Ga<sub>2</sub>O<sub>3</sub>. 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 In<sub>2</sub>O<sub>3</sub> due to Annealing at 1000 °C**Biserka Grzeta<sup>a</sup>, Emilija Tkalec<sup>b</sup>, Christian Goebbert<sup>c</sup>, Jasminka Popovic<sup>a</sup>, Vadim Ksenofontov<sup>d</sup>, Sergey Reiman<sup>d</sup>, Claudia Felser<sup>d</sup>, <sup>a</sup>Rudjer Boskovic Institute, P.O. Box 180, HR-10002, Zagreb. <sup>b</sup>Faculty of Chemical Engineering and Technology, University of Zagreb, Marulicev trg 20, HR-10000 Zagreb, Croatia. <sup>c</sup>ITN Nanovation, D-38820 Halberstadt. <sup>d</sup>Johannes Gutenberg-Universität, Staudinger Weg 9, D-55099 Mainz, Germany. E-mail: grzeta@irb.hr

Sn doped In<sub>2</sub>O<sub>3</sub> (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 InCl<sub>3</sub> and SnCl<sub>4</sub> [2]. The samples were additionally annealed at 1000 °C for 1 h, slowly cooled to RT and examined by XRD and <sup>119</sup>Sn Moessbauer spectroscopy. XRD revealed that the samples were isostructural with In<sub>2</sub>O<sub>3</sub> [3]. Lattice parameter *a* increased almost linearly with Sn-content from the value of 10.1215(5) Å for pure In<sub>2</sub>O<sub>3</sub> to 10.1319(4) Å for 14 at% Sn. While <sup>119</sup>Sn 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 Sn<sup>4+</sup> 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 In<sub>2</sub>O<sub>3</sub>, X-ray diffraction, Moessbauer spectroscopy

**P.11.10.11***Acta Cryst.* (2005). **A61**, C395**Push-Pull Mixed-Ligand d<sup>8</sup>-Metal Dithiolene Complexes**Luca Pilia<sup>a</sup>, Paola Deplano<sup>a</sup>, Cristophe Faulmann<sup>b</sup>, Andrea Ienco<sup>c</sup>, Carlo Mealli<sup>c</sup>, Maria Laura Mercuri<sup>a</sup>, Angela Serpe<sup>a</sup>, <sup>a</sup>DCLA, Università di Cagliari, Italy. <sup>b</sup>LCC-CNRS, Toulouse, France. <sup>c</sup>ICCOM-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 (C<sub>2</sub>S<sub>2</sub>)Ni(C<sub>2</sub>S<sub>2</sub>) core and two different terminal groups (R<sub>2</sub>pipdt=1,4-dialkyl-piperazine-3,2-dithione; R<sub>2</sub>timdt=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 ( $\beta$ ) indicated that some of the species are NLO chromophores, due the  $\pi$ -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 R<sub>2</sub>pipdt and R<sub>2</sub>timdt ligands. DFT calculations have been carried out to correlate geometries and electronic structures.  $\beta$  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  $\pi$ -electron density induced by dmit. The novel complex [Pd(Me<sub>2</sub>pipdt)(dmit)] has been obtained and shows negative solvatochromism. Its structural and electronic properties will be compared with those of the nickel analogue.

[1] Curreli S., Deplano P., Faulmann C., Ienco A., Mealli C., Mercuri M.L., Pilia L., Pintus G., Serpe A., Trogu E.F., *Inorg. Chem.*, 2004, **43**(16), 5069-5079.

**Keywords:** metal complexes, NLO, DFT

**P.11.11.1***Acta Cryst.* (2005). **A61**, C395**Structures of Perovskite-related layered A<sub>n</sub>B<sub>n</sub>O<sub>3n+2</sub>**Jonathan Guevarra<sup>a</sup>, Sander van Smaalen<sup>a</sup>, Nicola Rotiroti<sup>a</sup>, Frank Lichtenberg<sup>b</sup>, <sup>a</sup>Laboratory of Crystallography, University of Bayreuth, 95440 Bayreuth, Germany. <sup>b</sup>Institut für Physik, EKM, Experimentalphysik VI, Universität Augsburg, Universitätsstraße 1, 86135 Augsburg, Germany. E-mail: jonathan.guevarra@uni-bayreuth.de

Perovskite-related oxidic compounds A<sub>n</sub>B<sub>n</sub>O<sub>3n+2</sub> (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 ABO<sub>3</sub> perovskite-type structure with additional layers of oxygen separating the slabs of BO<sub>6</sub> 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 BO<sub>6</sub> 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., Griani M., Lichtenberg F., Herrnberger A., Mayr F., Mannhart J., *Phys. Rev. Lett.*, 2002, **89**, 236403.

**Keywords:** X-ray diffraction, perovskite, A<sub>n</sub>B<sub>n</sub>O<sub>3n+2</sub>

**P.11.11.2***Acta Cryst.* (2005). **A61**, C395-C396**Structural Phase Transition of La<sub>0.815</sub>Ba<sub>0.185</sub>MnO<sub>3</sub> studied by X-ray Diffraction and the Maximum Entropy Method**Nicola Rotiroti<sup>a</sup>, Rafael Tamazyan<sup>b</sup>, Sander van Smaalen<sup>a</sup>, Ya. Mukovskii<sup>c</sup>, <sup>a</sup>Laboratory of Crystallography, University of Bayreuth, Bayreuth, Germany. <sup>b</sup>Molecule Structure Research Centre, Yerevan, Republic of Armenia. <sup>c</sup>Moscow State Steel and Alloys Institute, Moscow, Russian Federation. E-mail: nicola.rotiroti@uni-bayreuth.de

La<sub>0.815</sub>Ba<sub>0.185</sub>MnO<sub>3</sub> (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<sub>0.815</sub>Ba<sub>0.185</sub>MnO<sub>3</sub> a metal-insulator transition and CMR take place at T<sub>c</sub>=251K [1,2]. A first-order structural phase transition takes place at T<sub>s</sub>≈196K. At the latter temperature, anomalies in both resistivity and magnetization temperature dependency have been observed. We