

Electronal, Electronic and Information Engineering, 2-1 Yamadaoka, Suita, Osaka, 565-0871, Japan, <sup>2</sup>Fukushima National College of Technology, 30 Nagao, Hirakamiarakawa, Iwaki, Fukushima 970-8034, Japan, <sup>3</sup>Institute of Laser Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan, <sup>4</sup>Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan, E-mail: matsukawa@cryst.eei.eng.osaka-u.ac.jp

4-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST) is a well-known organic nonlinear optical material for emitting high-power and broadband terahertz (THz) wave. However, it had nearly reported about the crystals of DAST-derivative materials and their properties as a THz wave source. In this study, we designed new DAST-derivative materials, grew these crystals, and investigated their THz-wave properties. We synthesized various DAST-derivative materials such as 1-methyl-4-{2-[4-hydroxyphenyl]ethenyl}pridinium p-toluenesulfonate (MC-pTS), new material named bis[1-methyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pridinium]terephthyanate (BDAS-TP), and so on. Then we prepared their solutions with methanol solvent, and grew their crystals by using slow-cooling process. Fig. 1 shows the obtained crystals of MC-pTS and BDAS-TP. By using a femtosecond laser, we found BDAS-TP crystal can generate broadband THz-wave.

[Acknowledgment]

This research was supported by the Global COE Program, "Center for Electronic Devices Innovation".

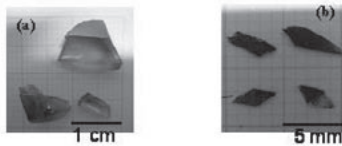


Fig.1 Crystals of DAST derivatives (a) MC-pTS (b) BDAS-TP

Keywords: laser and nonlinear optical materials, organic chemistry, crystal growth from solution

### P11.11.36

*Acta Cryst.* (2008). A64, C518

#### Neutron and X-ray powder diffraction investigation of $\text{LaMnO}_3$

Tapan Chatterji, Bachir Ouladdiaf, Paul F. Henry

Institut Laue-Langevin, Science, 6 rue Jolles Horowitz, Grenoble, Isere, 38042, France, E-mail: chatterji@ill.eu

The parent compound  $\text{LaMnO}_3$  of the hole-doped colossal magneto-resistance (CMR) materials crystallizes in the orthorhombic space group Pbnm. The structure consists of  $\text{MnO}_6$  octahedra that are distorted due to the Jahn-Teller effects. Below  $T_O = 750$  K  $\text{LaMnO}_3$  has an orbital ordered state that consists of the  $\text{Mn}^{3+}$  eg orbitals in an alternate staggered pattern in the a-b plane that repeats itself along the c axis. This type of orbital order induces A-type antiferromagnetic (AF) ordering below  $T_N = 141$  K and coexists with it. In the A-type AF phase the ferromagnetic a-b plane are stacked antiferromagnetically along the c-axis. We have investigated the orbital order-disorder transition in  $\text{LaMnO}_3$  by high temperature X-ray powder diffraction with synchrotron radiation and also neutron powder diffraction. The unit cell volume of  $\text{LaMnO}_3$  increases with increasing temperature and at higher temperature it starts decreasing in a narrow temperature range below  $T_O = 750$  K, and then undergoes a volume collapse at  $T_O$ . The Pbnm symmetry of  $\text{LaMnO}_3$  is retained above  $T_O$  although the unit cell becomes pseudo-cubic. We have constructed a theory of this phase transition by a model Hamiltonian involving the pseudo-spin of  $\text{Mn}^{3+}$  eg states, the staggered JT distortion and the volume strain coordinate. We also investigated the magnetoelastic effect at the antiferromagnetic phase transition

in  $\text{LaMnO}_3$  by neutron powder diffraction. The lattice parameters a decreases with temperature up to  $T_N = 141$  K and then abruptly starts increasing whereas the lattice b shows the opposite effect. The third lattice parameter c and the unit cell volume show only weak anomalies close to  $T_N$ . We interpreted these results in terms of a spin-lattice coupling Hamiltonian and have extracted the coupling constant.

Keywords: orbital ordering, antiferromagnetic ordering, magneto-elastic effect

### P11.11.37

*Acta Cryst.* (2008). A64, C518

#### Tuning magnetic interaction in orthorhombic neodymium-yttrium manganites $\text{Nd}_{1-x}\text{Y}_x\text{MnO}_3$

Sven Landsgesell, Dimitri Argyriou, Oleksandr Prokhnenko, Nadir Aliouane

HMI Berlin, SF2, Glienicke Str. 100, Berlin, Berlin, 14109, Germany, E-mail: landsgesell@hmi.de

By lowering the Mn-O-Mn bond angle in  $\text{LnMnO}_3$  with  $\text{Ln}=\text{La}-\text{Ho}$  the Neel-temperature decreases and at  $\text{Ln}=\text{Tb}$  the A-type antiferromagnet transforms to an incommensurate (IC) spin-spiral phase for  $\text{Ln}=\text{Gd}, \text{Tb}, \text{Dy}$ . The spin-spiral breaks both inversion and time reversal symmetry leading to a strong coupling between magnetism and ferroelectric polarization. We investigate the evolution of the crystal and magnetic structure from the A-type phase to the IC spin spiral phase by systematically replacing neodymium by yttrium in  $\text{NdMnO}_3$  resulting to a decrease of the tolerance factors to values similar to that for multiferroic  $\text{TbMnO}_3$ . One advantage of this approach is that the tolerance factor can be tuned and that neodymium and yttrium are not high neutron absorbing elements in sharp contrast to other rare earths like Gd, Dy and Eu. Compositions  $x=0.0$  to 0.6 have been prepared, neutron and x-ray powder diffraction patterns were measured as well as the magnetic properties. It can be shown that by decreasing the tolerance factor that way, similar effects can be seen as with varying the ionic size of the rare earth ions. For example we found that between  $0.4 < x < 0.6$  the incommensurate phase co-exists with the A-type antiferromagnetic phase and with  $x=0.6$  and higher the system is only incommensurate and seemingly multiferroic.

Keywords: manganites, multiferroics,  $\text{NdYMnO}_3$

### P11.11.38

*Acta Cryst.* (2008). A64, C518-519

#### Superstructures in $\text{RBaCo}_2\text{O}_{5.5}$ (R=Nd, Tb) as seen from reciprocal space mapping

Dmitry Chernyshov<sup>1</sup>, Ekaterina Pomjakushina<sup>2</sup>, Vladimir Pomjakushin<sup>3</sup>, Vladimir Dmitriev<sup>1</sup>

<sup>1</sup>SNBL at the ESRF, BP 220, Grenoble, Grenoble, 38043, France, <sup>2</sup>Laboratory for Developments and Methods, PSI Villigen, CH-5232 Villigen PSI, Switzerland, <sup>3</sup>Laboratory for Neutron Scattering, ETH Zurich / PSI Villigen, CH-5232 Villigen PSI, Switzerland, E-mail: dmitry.chernyshov@esrf.fr

In  $\text{RBaCo}_2\text{O}_{5.5}$  (R= rare earth element) the  $\text{Co}^{3+}$  ions can be found in either low spin state, an intermediate spin state or in a high spin state. Providing that the energy difference between these states is small, i.e.  $\sim k_B T$ , different electronic and vibrational degeneracy may lead, via an entropy factor, to a temperature induced spin-

state conversion. Ordering of the spin states is manifested in the corresponding superstructure reflections; these can be traced in a diffraction experiment as a function of external stimuli. By mapping reciprocal space with an area detector and synchrotron light, we have studied the temperature dependence of the superstructure reflections for  $\text{NdBaCo}_2\text{O}_{5.5}$  and  $\text{TbBaCo}_2\text{O}_{5.48}$ . We have found that above the metal-insulator transition there are two different Co ions in the asymmetric unit, one sitting in a pyramidal and one in an octahedral environment. Below the transition temperature there are four structurally different Co ions. This observation agrees with the "spin blockade" mechanism suggested for the metal-insulator transition in cobaltites. We also present results of structural analyzes illustrating how the corresponding powder diffraction measurements could easily overlook the correct structure. A symmetry analysis bracketing the observed phase transitions within the context of Landau theory is also given.

Keywords: cobaltites, spin transition, spin ordering

### P11.11.39

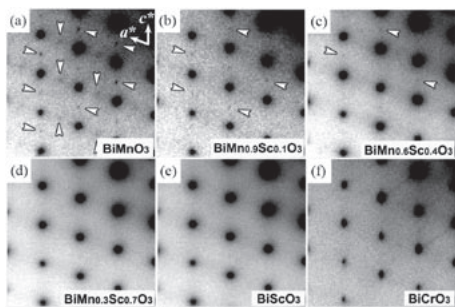
*Acta Cryst.* (2008). A64, C519

#### Investigation of the crystal symmetry of $\text{BiMnO}_3$ : Electron diffraction study

Tadahiro Yokosawa<sup>1</sup>, Alexei A Belik<sup>2</sup>, Toru Asaka<sup>1</sup>, Koji Kimoto<sup>1</sup>, Eiji Takayama-Muromachi<sup>2</sup>, Yoshio Matsui<sup>1</sup>

<sup>1</sup>National Institute for Materials Science, Advanced Nano Characterization Center, Namiki 1-1, Tsukuba, Ibaraki prefecture, 305-0044, Japan, <sup>2</sup>National Institute for Materials Science (NIMS), Advanced Nano Materials Laboratory, Namiki 1-1, Tsukuba, Ibaraki prefecture, 305-0044, Japan, E-mail: YOKOSAWA.Tadahiro@nims.go.jp

$\text{BiMnO}_3$  has been considered as a multiferroic material due to the ferroelectric and ferromagnetic properties. The crystal symmetry is, however, controversial today. We investigated the crystal symmetry of  $\text{BiMnO}_3$  by Convergent-Beam and Selected-Area Electron Diffraction (CBED and SAED, respectively). CBED, which was used in order to discriminate the crystal axes of  $\text{BiMnO}_3$ , showed that  $\text{BiMnO}_3$  belongs to space group  $C2/c$ . In the  $[010]$  SAED pattern, however, the very weak but sharp  $h0l$  ( $l=2n+1$ ) reflections were observed indicating the noncentrosymmetric long-range ordered structure ( $C2$ ) [1]. This implies that the weak reflections had quite little influence on the CBED patterns [2]. The  $h0l$  ( $l=2n+1$ ) reflections could not be detected in structurally related  $\text{BiScO}_3$  and  $\text{BiCrO}_3$  indicating centrosymmetric  $C2/c$ , respectively [1]. This strongly suggests that the noncentrosymmetric long-range ordered structure ( $C2$ ) of  $\text{BiMnO}_3$  is attributed not only to  $\text{Bi}^{3+}$  ions with lone electron pair but also to  $\text{Mn}^{3+}$  ions, that is, to correlation between  $\text{Bi}^{3+}$  and  $\text{Mn}^{3+}$  ions. [1]T. Yokosawa, et al. *Phys. Rev. B* **77**, 024111 (2008) [2]M. Tanaka, M. Terauchi, and T. Kaneyama, *CBED II* (JEOL, Tokyo, 1988), pp. 120-139.



Keywords: ferroantiferro-magnetic ferroelectrics, perovskite oxides, electron diffraction

### P11.11.40

*Acta Cryst.* (2008). A64, C519

#### Structural and magnetic phase transitions in the complex perovskite systems $\text{BiMn}_7\text{O}_{12}$ and $\text{LaMn}_7\text{O}_{12}$

Gwenaëlle Rousse<sup>1</sup>, Edmondo Gilioli<sup>2</sup>, Pierre Bordet<sup>3</sup>, Gilles Andre<sup>4</sup>, Andrea Gauzzi<sup>1</sup>

<sup>1</sup>Universite Pierre et Marie Curie, Institut de Mineralogie et de Physique de la Matière condensée (IMPMC), Campus Boucicaud, 140 rue de Lourmel, Paris, PARIS, 75015, France, <sup>2</sup>IMEM, CNR, Are delle Scienze 37/A, 43100 Parma, Italy, <sup>3</sup>Institut Neel, CNRS, 25 rue des Martyrs, 38042 Grenoble, France, <sup>4</sup>Laboratoire Leon Brillouin, CEA, E-mail: rousse@impmc.jussieu.fr

By means of neutron powder diffraction as a function of temperature, we have investigated the nuclear and magnetic structures of the new systems  $(\text{BiMn}_3^{3+})(\text{Mn}_3^{4+})\text{O}_{12}$  and  $(\text{LaMn}_3^{3+})(\text{Mn}_3^{4+})\text{O}_{12}$ . Single-phase powder samples of both phases were recently synthesized under high pressures at the IMEM-CNR in Parma. In both systems, the A' cation is trivalent, thus all of the Mn B-cations are expected to be trivalent. Both systems crystallize in the  $A_3B_4\text{O}_{12}$  complex perovskite structure consisting of a pseudo-cubic network of corner-shared  $\text{BO}_6$  octahedra. This system may display a rich manifold of charge, spin and orbital orderings characteristic of mixed-valence systems. In both systems, we have determined precisely the nuclear and magnetic structures as a function of temperature, between room temperature and 2K. We have observed two magnetic transitions at low temperature in the La compound, involving crystallographically different Mn ions. Between 65K and 20K, the propagation vector  $k$  is  $(0,0,0)$ , and only the Mn ions in the B-site are ordered. Below 20K, additional magnetic reflections appear, the lattice is no longer body centered, and magnetic moments of manganese atoms belonging to the A site are ordered. The magnetic structure has been solved by simulated annealing techniques, with help of symmetry analysis. It will be discussed in comparison with the Na analog which had been studied before. For the Bi compound, the effect of the lone pair of Bi on the structure will be discussed, as well as the magnetic structures observed at low temperature.

Keywords: magnetic structures, perovskite structures, neutron powder diffraction

### P11.11.41

*Acta Cryst.* (2008). A64, C519-520

#### Coupling of Tb- and Mn-magnetic orders in multiferroic $\text{TbMnO}_3$

Oleksandr Prokhnenko<sup>1</sup>, Ralf Feyerherm<sup>1</sup>, Maxim Mostovoy<sup>2</sup>, Nadir Aliouane<sup>1</sup>, Esther Dudzik<sup>1</sup>, Anja U.B. Wolter<sup>1</sup>, Andrey Maljuk<sup>1</sup>, Dimitri N. Argyriou<sup>1</sup>

<sup>1</sup>Hahn Meitner Institute, Glienickestr. 100, Berlin, 14109, Germany, <sup>2</sup>Zernike Institute for Advanced Materials, University of Groningen, 9747 AG Groningen, Netherlands, E-mail: prokhnenko@hmi.de

While ferroelectricity and magnetism are chemically incompatible, it has recently been shown that inversion and time-reversal symmetry can be broken simultaneously if magnetic spins order in a cycloidal arrangement as in  $\text{RMnO}_3$ . It has been also shown that although the magnetic ordering of Mn-spins drives multiferroicity, R-ions strongly modulate it and thus significantly influence multiferroic properties. Irrespective of the mechanism that drives multiferroic behavior, the magnetic coupling between R- and Mn-spins needs to be understood in order to arrive at a detailed and quantitative model of multiferroics. Here we report on diffraction measurements which demonstrate that the Tb- and Mn- magnetic ordering in multiferroic  $\text{TbMnO}_3$  remain