

**FA2-MS16-P05**

**Organosilyl and organotin plenary Lindqvist polyoxometalates derivatives.** Mongi Debbabi, Fatma Bannani Driss. *Laboratoire de physico-chimie des Matériaux, Faculté des Sciences de Monastir, Tunisie.*  
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Polyoxometalates form a class of compounds that is unique in its versatile properties and applications. Despite of enormous work focused on the functionalisation of POMs done so far, synthesis of derivatized polyoxoxanions is still a challenging and demanding task.

We are particularly interested in the in the derivatisation of Lindqvist type polyoxoanions with organosilyl and organotin moieties. Such reactions require two steps; the first one consists of the synthesis of dimeric  $(n\text{Bu}_4\text{N})_4[(\text{MW}_5\text{O}_{18})_2\text{O}]$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) as starting material;  $(n\text{Bu}_4\text{N})_4[(\text{TaW}_5\text{O}_{18})_2\text{O}]$  was characterized by IR spectroscopy and single crystal X-ray diffraction. It crystallizes in the orthorhombic system, space group *Pbnm* with lattice parameters  $a = 15.7981(14)$ ,  $b = 17.939(3)$ ,  $c = 35.216(6)\text{Å}$ ,  $V = 9980\text{ Å}^3$  and  $Z = 4$ .

The grafting of organic moieties onto the dimeric forms leads to the formation of monomeric plenary Lindqvist hybrids  $(n\text{Bu}_4\text{N})_2[\text{MW}_5\text{O}_{18}\text{EOR}_3]$  ( $\text{E} = \text{Si}, \text{Sn}$ ). These derivatives were characterized in the solid state by IR and in solution by multinuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{119}\text{Sn}$ ,  $^{183}\text{W}$ ). The crystallographic study of  $(n\text{Bu}_4\text{N})_2[(\text{W}_5\text{O}_{18}\text{Ta}(\text{O})\text{SiPh}_3)]$  indicates that the structure of the POM is conserved and  $\{\text{SiPh}_3\}^+$  is grafted selectively on the surface of the polyanion through the terminal  $\text{O}_T\text{-Ta}$  oxygen atom.

**Keywords:** polyoxometalates, crystal structures, NMR spectroscopy

**FA2-MS16-P06**

**Pressure-Induced Isostructural Phase Transformation in  $\gamma\text{-B}_{28}$ .** N. Dubrovinskaia<sup>b,c</sup>, E. Yu. Zarechnaya<sup>a</sup>, R. Caracas<sup>d</sup>, M. Merlini<sup>e</sup>, M. Hanfland<sup>f</sup>, Y. Filinchuk<sup>f</sup>, D. Chernyshov<sup>f</sup>, V. Dmitriev<sup>f</sup>, L. Dubrovinsky<sup>a</sup>. <sup>a</sup>*Bayerisches Geoinstitut, Universität Bayreuth, Germany.* <sup>b</sup>*Mineralphysik, Institut für Geowissenschaften, Universität Heidelberg, Germany.* <sup>c</sup>*Lehrstuhl für Kristallographie, Physikalisches Institut, Universität Bayreuth, Germany.* <sup>d</sup>*Centre National de la Recherche Scientifique, Ecole Normale Supérieure de Lyon, Laboratoire de Sciences de la Terre, France.* <sup>e</sup>*ESRF, Grenoble, France.* <sup>f</sup>*Dipartimento di Scienze della Terra, Università degli Studi di Milano, Italy.*  
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sostructural phase transformations (ISPhTs) are particular cases of isosymmetric transformations and include discontinuous isostructural transitions and crossovers. They are rare, intriguing phenomena in solids often associated with a significant volume collapse, giant magneto-elastic coupling, or negative thermal expansion. So far ISPhTs were reported for heavy elements and their compounds with complex electronic and/or magnetic structures. We have studied the high-pressure boron phase  $\gamma\text{-B}_{28}$  by means of *in situ* Raman spectroscopy up to 105 GPa, single-crystal X-ray diffraction in diamond anvil cells above 65 GPa and first-principles calculations. The discontinuous behavior of the Raman modes and the abrupt changes in the compressional behavior of  $\gamma\text{-B}_{28}$  are manifestations of the isostructural phase transformation at

about 40 GPa. The combined experimental and *ab initio* theoretical analysis of the structural and vibrational properties of  $\gamma\text{-B}_{28}$  suggest that the ISPhT under compression is due to the changes of the polarity of the covalent bonds between the boron atoms in the complex quasimolecular structure of  $\gamma\text{-B}_{28}$ .

**Keywords:** boron, phase transitions in solids, high-pressure crystallography

**FA2-MS16-P07**

**Domain redistribution in  $\text{SrTiO}_3$ .** Holger Gibhardt<sup>a</sup>, Jakob Sidoruk<sup>a</sup>, Jeannis Leist<sup>a</sup>, Klaudia Hradil<sup>a</sup>, Martin Meven<sup>b</sup>, Götz Eckold<sup>a</sup>. <sup>a</sup>*Institut für Physical Chemistry, Georg August University Göttingen, Germany.* <sup>b</sup>*Institute for Crystallography, RWTH Aachen and FRM II, Garching, Germany.*  
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At ambient temperatures strontium titanate ( $\text{SrTiO}_3$ ) has a cubic perovskite structure. Below 105 K the antiphase rotation of adjacent oxygen octahedra leads to an antiferrodistortive transition into a tetragonal phase [1]. During this transformation three different kinds of domains are formed with their tetragonal axes along each of the cubic principal axes. A ferroelectric phase like in the isostructural barium titanate ( $\text{BaTiO}_3$ ) is not observed, even at low temperatures. Long range ferroelectric order is suppressed by quantum fluctuations but can be induced by applying an external electric field [2].

The domain distribution can be changed considerably by applying uniaxial mechanical stress [3]. Since the tetragonal distortion corresponds to a  $c/a$ -ratio larger than unity, stress along the [110]-direction results in the preferred formation of domains with a tetragonal axis along [001]. Recently, we reported that even an electric field leads to a redistribution of tetragonal domains [4].

In this contribution we present the results of neutron scattering experiments using the diffractometer HEIDI at the FRM II neutron source in Garching. The intensities of a set of 15 superlattice reflections originating from combinations of different domains were determined and fitted to a structure factor model. This yields a quantitative determination of the domain distribution in  $\text{SrTiO}_3$  as a function of temperature, uniaxial stress and electric field.

Even untreated samples did not show a uniform domain distribution and consisted to almost 50 % of  $z$ -domains. This may be a result of residual stresses originating in crystal growth or sample preparation. Mechanical stress applied along the [110]-direction caused an increase of  $z$ -domains and only 15 MPa were sufficient to obtain almost monodomain samples. The changes were temperature independent and irreversible. Even after heating the sample above 120 K the same domain distribution was observed in subsequent measurements. An electric field along [001] showed the opposite effect and favoured the reversible formation of  $x$ - and  $y$ -domains. The redistribution was temperature dependent and increased on cooling. A complete suppression of  $z$ -domains was observed when the field induced ferroelectric phase was entered. The simultaneous application of stress and field showed that it is impossible to obtain monodomain samples. Moreover, the present results show that the polar axis of the field induced ferroelectric phase is always perpendicular to the tetragonal axes, corresponding to orthorhombic symmetry.

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**Keywords:** domains, electric fields, mechanical stress

#### FA2-MS16-P08

**Monoclinic superstructure of mullite-type  $KAl_9O_{14}$ .**  
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The chemical composition of the Al, Si-mullites is given by the general formula  $Al_2(Al_{2+2x}Si_{2-2x})O_{10-x}$ . The amount of  $Si^{4+}$  substituted by  $Al^{3+}$  is correlated with the sum of oxygen vacancies necessary to retain charge balance. In mullite-type aluminates  $X^{2-2x}Al_2(Al_4)O_{10-x}$  negative charge is compensated by incorporation of equivalent number (2-2x) positively charged X cations [1].

Single crystals of  $KAl_9O_{14}$  (or  $K_{0.67}Al_6O_{9.33}$ ) were grown using a flux method. Purity of the sample was confirmed by SEM-EDX analyses. Colourless needle-like prisms of  $KAl_9O_{14}$ , some as long as 1 cm, show with cross-polarised light twin planes perpendicular to the needle axis. The structure was determined from single-crystal data and refined to a residual  $R|F| = 0.031$ . The compound crystallizes in the monoclinic space group  $P2_1/n$  ( $a = 8.1937(6)$ ,  $b = 7.6734(6)$ ,  $c = 8.7930(6)$  Å,  $\beta = 110.747(6)^\circ$ ,  $V = 516.99(7)$  Å<sup>3</sup>,  $Z = 2$ ). A detailed analysis based on oriented sections of reciprocal space revealed that the crystal is also subject to twinning by partial merohedry which was accounted for during the refinement. Furthermore, distinct one-dimensional diffuse scattering parallel to  $c^*-(a^*/3)$  could be observed.

Crystals of  $KAl_9O_{14}$  have a typical mullite-type structure with linear edge sharing  $AlO_6$  octahedral chains connected with inner-chain groups comprising two  $AlO_4$  tetrahedra and one  $AlO_5$  trigonal bipyramid. The 4+1 coordinated aluminium has four shorter (1.75-1.86 Å) and one longer bond (2.16 Å) to oxygen atoms. K-atoms are located in the centre of cavities originating from oxygen vacancies. Differences between the calculated powder diffraction pattern of this structure and known powder diagrams of  $K_{0.67}Al_6O_{9.33}$  [2] clearly confirmed that this structure is a new polymorph.

The monoclinic superstructure of  $KAl_9O_{14}$  can be transformed to a  $3 \times c$  orthorhombic supercell ( $a = 7.69$  b = 7.68 c = 8.82 Å). A similar ( $3 \times a$ ) superstructure was postulated for the 4:1 mullite earlier [3].

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**Keywords:**  $KAl_9O_{14}$ , mullite, superstructure

#### FA2-MS16-P09

**Structural characterization of a new Pb/Sr based ferri-manganite presenting incommensurate shear structure by combining different techniques of transmission electron microscopy.**

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Perovskite related iron and manganese based Crystallographic Shear (CS) structures have first been discovered in the Pb rich part of the Pb-Sr-Fe(Mn)-O diagram. Recent studies on the CS perovskite  $PbFeO_{2.5}$  [1], [2], [3] evidenced the role of the lone pair cation in the shear process and a large family of compounds  $Pb_{4m+3n}Fe_{4(m+n)}O_{10+9n}$  with different shear  $1/2[110]_p(h0l)_p$  ( $p$  denotes perovskite) mechanisms has been defined. The  $1/2[110]_p(\bar{3}05)_p$  structure of  $Pb_{18}Fe_{20}O_{48}$  ( $Pb_{0.9}Fe_{0.24}$ ) [1] will be used as a comparative example to describe the structure of our Pb-site deficient perovskite-like compound.

The latter is a ferri-manganite synthesized for the composition  $Sr_{0.61}Pb_{0.18}(Fe_{0.75}Mn_{0.25})O_{2.29}$  and its new modulated CS structure, related to perovskite, was characterized by transmission electron microscopy. The Selected Area Electron Diffraction study allowed to describe the structure in a C centered monoclinic supercell with the parameters :  $a_m = 27.595(2)$  Å,  $b_m = 3.8786(2)$  Å,  $c_m = 13.3453(9)$  Å and  $\beta = 100.125(5)^\circ$ , refined from powder X-ray diffraction data. The structure determined from the High Resolution Transmission Electron Microscopy (HRTEM) and High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF STEM) studies corresponds to a  $1/2[110]_p(203)_p$  CS structure, following the concept of a phasoid with two coexisting variants ("1" and "2") with the same monoclinic unit cell. The difference takes place at the translational interface, creating two local phases coexisting in the same particle with either double or single tunnels, where Pb atoms are likely located [4]. The incommensurability phenomena are associated with the formation of defective boundaries through structural unit groups, which are common part of the normal sequences encountered in the two variants, leading to a slight misalignments of the "1" and "2" monoclinic supercells along  $\bar{a}_m$  [5].

The structural resolution carried out from the precession electron diffraction data allowed to identify the 2 monoclinic phases "1" and "2" with the good positions of the different cations.

This compound exhibits an insulating behavior coupled with a strong antiferromagnetism with the presence of a small coercive field hysteresis [5].

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**Keywords:** structural characterization, transmission electron microscopy, incommensurate modulated structure