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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 polyoxoanions 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 (nBu4N)2[(MW5O18EOR3] (E= Si, Sn) as starting material; (nBu4N)4[(TaW5O18)2O] 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)Å, V = 9980 Å3 and Z = 4.

The grafting of organic moieties onto the dimeric forms leads to the formation of monomeric plenary Lindqvist hybrids (nBu4N)4[(MW5O18EOR3] (E= Si, Sn). These derivatives were characterized in the solid state by IR and in solution by multinuclear NMR (1H, 13C, 29Si, 119Sn, 183W). The crystallographic study of (nBu4N)4[(TaW5O18)2O] indicates that the structure of the POM is conserved and the methyl group is grafted selectively on the surface of the polyanion through the terminal O-Ta oxygen atom.

Keywords: polyoxometalates, crystal structures, NMR spectroscopy


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Isostructural phase transformations (ISPhts) are particular cases of isosymmetric transformations and include discontinuous isstructural 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 or magnetic structures. We have studied the high-pressure boron phase γ-B28 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 γ-B28 are manifestations of the isostrophic phase transformation at about 40 GPa. The combined experimental and ab initio theoretical analysis of the structural and vibrational properties of γ-B28 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 γ-B28.

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


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At ambient temperatures strontium titanate (SrTiO3) has a cubic perowskite 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 isosstructural barium titanate (BaTiO3) 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 FIRM 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 SrTiO3 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 supression 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.

Keywords: domains, electric fields, mechanical stress

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Monoclinic superstructure of mullite-type KAlO\(_{14}\)-
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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\(^{IV}\) substituted by Al\(^{III}\) 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 (2-2\(x\)) positively
charged X cations [1].

Single crystals of KAlO\(_{14}\) (or K\(_{0.67}\)Al\(_{6}\)O\(_{9.33}\)) are grown using a
flux method. Purity of the sample was confirmed by SEM-
EDX analyses. Colourless needle-like prisms of KAlO\(_{14}\), 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, \(\beta = 110.747(6)\), V = 516.99(7) Å\(^3\), \(Z = 2\).

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.

Crysstals of KAlO\(_{14}\) 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\(_3\) trigonal bipyramid. The 4+1 coordinated aluminum 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\(_{6}\)O\(_{9.33}\) [2] clearly
confirmed that this structure is a new polymorph.

The monoclinic superstructure of KAlO\(_{14}\) 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].

[1] Schneider H., Konamerni S., Mullite, WILEY-VCH, Weinheim,
79, 983.

Keywords: KAlO\(_{14}\), 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.

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 system. 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\(_{57}\)Fe\(_{60}\)O\(_{48}\) with different shear
1/2\(1[10]_p(h0l)\) \(p\) (\(p\) denotes perovskite) mechanisms has been
defined. The 1/2\(1[10]_p(305)_p\) structure of Pb\(_{18}\)Fe\(_{20}\)O\(_{48}\)
(Pb\(_{0.16}\)Fe\(_{2.4}\)) [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\(_{0.67}\)Pb\(_{18}\)Fe\(_{20}\)Mn\(_{2}\)O\(_{48}\) 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 :
\(a_0 = 27.592(2)\) Å, \(b_0 = 3.87862(2)\) Å, \(c_0 = 13.3453(9)\) Å and
\(\beta = 100.125(5)\) °, refined from powder X-ray diffraction data.
The structure determined from the High Resolution
Transmission Electron Microscopy (HRTEM) and High Angle
Anamolular 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
phason 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 \(a_0\) [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
coeffective field hysteresis [5].


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