

a combination of scientific methods that had never been applied jointly to explore and clarify the thermal decomposition behaviour of this material.¹ Although monoalkylamines are usually employed as templates for the synthesis of titanium phosphate metastable phases, the structural features of γ -titanium phosphate alkylamine-intercalated compounds only recently have been reported.² Key to the full elucidation of the structure of the materials was the combination of XRD and NMR evidence with theoretical calculations of ¹H NMR chemical shifts. Since the great success of carbon nanotubes in 1991, interest in low-dimensional nanomaterials has fuelled a spectacular and unusual activity. Nowadays the nanotubes are not only made of carbon but also of inorganic materials, many of which are related with previously well-known layered structures. Organic-inorganic hybrid nanotubes based on the γ -titanium phosphate structure spaced with trialkylamines have been prepared by using microemulsion-mediated solvothermal and microwave-assisted methods. The interlayer distance in the inorganic sheets of the nanotube can be controlled by both the alkyl chain length and the amount of the amine template. All nanotubes obtained are open-ended with concentric cylinders, i.e., layers that fold and close within themselves. The possible reason for having this morphology seems to be related to the combination of two factors: *i*) the interaction between the nitrogen of trialkylamine molecules and the hydrogen belonging to inorganic skeleton that seeks to be maximum, and *ii*) the pseudo-conical geometry of the trialkylamine molecules that limits the number of accessible acid centers. In this way, the number of H-N links will depend on the length of the alkyl chain.³ In conclusion, studies using diffraction methods in tandem with high-resolution NMR spectroscopy should provide valuable information on the local environment in the inorganic-organic materials, including new γ -titanium phosphate based nanotubes.

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Polar atomic displacements in multiferroics by anomalous x-ray diffraction. Eduardo Granado^{a,b}, Carla Azimonte^{a,b}, Hirotoshi Terashita^{a,b}, Soonyong Park^c, Sang-Wook Cheong^c. ^a*Institute of Physics, University of Campinas - UNICAMP Campinas, Brazil.* ^b*Brazilian Synchrotron Laboratory – LNLS Campinas, Brazil.* ^c*Center for Emergent Materials and Department of Physics, Rutgers University Piscataway, USA.*
E-mail: egranado@ifi.unicamp.br

The minute polar atomic displacements in multiferroics are shown to be within the reach of crystallography. In these materials, electric polarization is not the main order parameter, rather appearing as a by-product of some other ordering. In particular, the magnetism-driven ferroelectrics (or type-II multiferroics) have attracted great attention since the coupling between electrical and magnetic order parameters offers the possibility of controlling electrical properties with magnetic

fields and vice-versa. Here, a non-conventional methodology with anomalous x-ray diffraction is employed to investigate the small atomic displacements in DyMn₂O₅ with giant magnetoelectric coupling and two distinct Mn³⁺ and Mn⁴⁺ sites [1]. Intensity differences of a selected Bragg reflection were measured as the direction of electric polarization is switched by a poling field. A significant differential effect, which is strongly enhanced at energies near and above the Mn *K*-edge, was observed near and below the ferroelectric transition temperature, $T_c \sim 40$ K. The direct participation of ionic displacements in the ferroelectric polarization, particularly the Mn³⁺ sublattice, is demonstrated, dismissing a purely electronic mechanism for the multiferroicity.

[1] Azimonte C.; Granado E.; Terashita H.; Park S.; Cheong S.-W. *Phys. Rev. B* 81, 012103 (2010).

Keywords: multiferroics, Friedel pairs, magnetoelectrics.

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XRD, XAS and DFT study of the multiferroic mixed-valence compound YMn₂O₅. Tilmann Leisegang^a, Torsten Weißbach^a, Falk Wunderlich^a, Hartmut Stöcker^b, Matthias Zschornak^a, Richard Boucher^c, Sibylle Gemming^d, Dirk C. Meyer^b. ^a*Institut für Strukturphysik, Technische Universität Dresden, Germany.* ^b*Institut für Experimentelle Physik, Technische Universität Bergakademie Freiberg, Germany.* ^c*Institut für Werkstoffwissenschaften, Technische Universität Dresden, German.* ^d*Institut für Ionenstrahlphysik und Materialforschung, Forschungszentrum Dresden-Rossendorf, Germany.*
E-mail: leisegang@physik.tu-dresden.de

YMn₂O₅ crystallizes in the structure type of the orthorhombic RMn₂O₅ class of oxides (*R*... rare earth). It shows a series of antiferromagnetic phases where several of them are also ferroelectric. This makes YMn₂O₅ an interesting material for its application in sensors or for data storage devices. By substituting another transition metal (*TM*) for Mn the materials' magnetic properties can be tuned to meet specific requirements. Since the Mn atoms occupy two non-equivalent Wyckoff sites within the unit cell, the system can be characterized as a mixed-valence compound. This is expected to have an impact on the substitution behaviour.

We investigated the substitution of Fe for Mn. Consequently, a series of YMn_{2-x}Fe_xO₅ nano-crystalline powder samples with $x = 0, 0.5, \text{ and } 1$ were synthesized by a modified citrate precursor technique. We utilized powder X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) as well as quantum theoretical modelling, using density functional theory (DFT), in order to study the two non-equivalent *TM* sites within the orthorhombic crystal structure. The short-range order, as well as the valence state, of the respective *TM* is determined quantitatively.

From XAS analysis it is concluded that the Fe³⁺ ions occupy the *4h* Wyckoff site only. Differences of the Mn-XAS spectra with x are interpreted in terms of changes of the dipole transitions to *4p* final states. Since only one Wyckoff site is involved the experimentally observed limit of phase stability, to a maximum amount of $x = 1$, can be explained. DFT calculations support the experimental findings on basis of the total energy of the different possible electronic configurations. Crystal field effects are identified to be responsible for the site

selective substitution of Fe for Mn. From magnetic measurements a general increase of the magnetic ordering temperature with increasing x , as well as multi and single-phase magnetic behaviour, is observed. A correlation with the crystal structure will be given.

Keywords: mixed-valence oxides, XRD, XAS

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Cellular Automata Modeling of Complex Inorganic Crystal Structures

Sergey V. Krivovichev^a, Vladislav V. Gurzhiy^a, Ivan G. Tananaev^b, Boris F. Myasoedov^b
^aDepartment of Crystallography, St. Petersburg State University, Russia. ^bInstitute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Russia.
 E-mail: skrivovi@mail.ru

Cellular automata (CA) have been introduced for simulation of self-reproductive biological systems [1] and have attracted considerable attention as a possible environment for modeling of a broad range of physical objects and processes [2], in particular, of periodic growth of complex chemical structures [3, 4]. From the formal point of view, CA is defined as a collection of five basic components:

$CA := \langle Z, S, N, f, B \rangle$,

where Z is a lattice (discrete working space of the CA consisting of cells; the simplest example is a 2-D plane filled by square cells);

$S = \{0, 1, 2, \dots\}$ is a finite number of values that the cells may take (usually, these values are associated with colors, e.g. $S = \{0, 1\}$ characterizes a binary (2-color) CA);

$N = \{-k_1, -k_1+1, \dots, -1, 0, 1, \dots, k_2-1, k_2\}$ is a neighborhood of CA action (for 1-D CA the value of the cell x_0 at the time $t = 1$ is determined by the values of k_1 and k_2 cells on the left and right sides at the time $t = 0$ (in simplest case, the neighborhood is symmetrical $k_1 = k_2 = 1$ and has a radius $k_0 = 1$, i.e. it consists of three cells ($k = 3$): x_{-1}, x_0, x_1 ; the value of the cell x_0 at the time $t = 1$ is determined by the values x_{-1}, x_0, x_1 at the time $t = 0$);

f is a local transition function that works for a certain neighborhood (usually written as a set of rules of the form $010 \rightarrow 1$;

B is a boundary conditions.

Since crystal structures are periodic by definition, their growth and topology can be described using a special class of CA that produce repetitive patterns.

In this contribution, we will construct CA models of such various classes of inorganic structures as uranyl selenates and iron sulfides. One of remarkable results of CA applications in crystal chemistry is that *the same* CA may generate *different* structural topologies. The resulting topology is determined by the initial conditions, i.e. by the structure of the first row. In the language of chemistry, this means that molecular-level growth mechanism of uranyl selenate layers is the same and the topology of the structure is controlled by the structure of nucleus spontaneously formed in solution.

In addition, application of CAs allows to predict possible topologies that may form in specific system. It also provides a computational basis for studying complexity and dynamics of topologically and chemically similar structures forming under similar physico-chemical conditions.

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Elastic anomalies and precursor effects in CBN and Ce:CBN relaxor ferroelectrics.

Chandra Shekhar Pandey^a, Jürgen Schreuer^a, Manfred Burianek^b, Manfred Mühlberg^b. ^aInstitut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, Germany. ^bInstitut für Kristallographie, Universität zu Köln, Germany.

E-mail: chandrashekhar.pandey@ruhr-uni-bochum.de

Ferroelectric materials are widely investigated because of their often promising electro-optic, pyroelectric, piezoelectric and photorefractive properties. $Ca_xBa_{1-x}Nb_2O_6$ (CBN-x) and cerium doped $Ca_xBa_{1-x}Nb_2O_6$ (Ce:CBN-x), both relaxor ferroelectric materials crystallizing in the partially filled tetragonal tungsten bronze (TTB) structure type, provide excellent alternatives to strontium barium niobate (SBN) for device applications because of their relatively high Curie temperature ($T_C = 264^\circ\text{C}$ for $x = 0.28$ for undoped and $T_C = 200^\circ\text{C}$ for Ce-doped CBN with $x = 0.28$).

Here we report on the anomalous elastic behaviour and precursor effects of undoped CBN-28 and Ce:CBN-28 single crystals grown by the Czochralski method as determined between room temperature and 1323 K employing resonant ultrasonic spectroscopy (RUS).

The temperature evolution of the elastic constants c_{ij} in the paraelectric phase (point symmetry group 4/mm) of Ce:CBN-x shows pronounced anomalies like in undoped CBN-28 [1]. Doping with Ce leads to a stiffening of all elastic constants of CBN-28. Below about 900 K all resonances of the freely vibrating samples show rapid softening when approaching T_C . The onset of elastic softening is frequency dependent. The deviations from Cauchy relations indicate predominance of ionic bonding at high temperatures. When approaching T_C directional bonding contributions become more and more important along the tetragonal axis. In the ferroelectric phase strong ultrasound dissipation effects appear which are probably related to interactions between sound waves and ferroelectric domain walls.

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Keywords: calcium barium niobate, ferroelectric transition, elasticity