

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.

[1] S. García-Granda, S.A. Khainakov, A. Espina, J.R. García, G.R. Castro, L. Mafra, C. Coelho, J. Rocha, *Inorg. Chem.*, 49(6), 2630-2638, (2010). [2] L. Mafra, J. Rocha, C. Fernández, G.R. Castro, S. García-Granda, A. Espina, S.A. Khainakov, J.R. García, *Chem. Mater.*, 20, 3944, (2008). [3] J.A. Blanco, S.A. Khainakov, O. Khainakova, J.R. García, S. García-Granda, *Phys. Status Solidi C*. DOI: 10.1002/pssc.200881701. (2009)

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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.*
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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).

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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.*
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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 $x=0, 0.5$, 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