materials. Surprisingly, however, during the last decade nearly no interest in the melilites as optical materials is documented in literature. In a recent study of nonlinear-laser properties of $Ba_2MgGe_2O_7$ [1] we found that germanate crystals with non-centrosymmetric melilite-type structure can manifest numerous attractive $\chi^{(2)}$- and $\chi^{(3)}$-interactions with good prospects of their use in experiments of modern laser physics and nonlinear optics. In the present contribution we summarize the results of our investigations of linear optical properties and of stimulated Raman scattering (SRS) of further germanates $Ba_2ZnGe_2O_7$, $Sr_2MgGe_2O_7$ and $Sr_2ZnGe_2O_7$, which all possess an unmodulated melilite-type structure. All four melilite crystals allow the generation of a lasing comb of approximately one octave bandwidth on pumping at $\lambda_{fl} = 1.06415$ μm, arising from a SRS-promoting vibration mode at ~770 – 780 cm^{-1}, which corresponds to the symmetrical stretching mode $\nu_s(GeO_3)$ of the $[Ge_2O_7]$ unit. In addition, for $Ba_2ZnGe_2O_7$ a second mode, $\delta_s(GeO_3)$, acts as a further SRS-promoting mode. For all four investigated germanate melilites numerous rather efficient $\chi^{(2)}$-, $\chi^{(3)}$-, and cascaded $\chi^{(3)} \leftrightarrow \chi^{(2)}$- photon-photon and photon-phonon parametric interactions are observed. While these phenomena are quite similar for the four germanate melilites their $\chi^{(1)}$-based properties (i.e. refractive indices and their dispersion) depend markedly on the chemical composition of the crystals. Going hand in hand with this, the phase matching possibilities for SHG (second harmonic generation) and SFG (sum frequency generation) processes vary within a range from SHG phase matching (SHG-pm) in the visible range ($Ba_2MgGe_2O_7$) to SHG-pm in near IR ($Sr_2MgGe_2O_7$ and $Ba_2ZnGe_2O_7$) to no possibility for SHG-pm for $Sr_2ZnGe_2O_7$. The latter crystal, however, is characterized by an iso-index point [2-4]. The diversity of optical properties of the germanate melilites, together with their nonlinear optical manifestations classifies this crystal family as an attractive group of optical materials.

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Keywords: melilites, linear optical properties, nonlinear optics

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Li_xFeO_2 as battery cathode material: Li^+/vacancy patterns and reaction energies. Michele Catti, Mercedes Montero-Campillo. *Dept. of Materials Science, University of Milano Bicocca, Italy.*
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More environment-friendly and less expensive cathode materials have been extensively sought to replace $LiCoO_2$ in lithium batteries. An attractive candidate is $LiFeO_2$, showing a complex polymorphism; some of its phases were considered in the past as active electrochemical materials [1,2]. We have undertaken a combined crystallographic (neutron diffraction) and theoretical (ab initio simulations) study of this system, to elucidate some aspects left open by electrochemical measurements. Preliminary results obtained on the β'

(monoclinic) and γ (tetragonal) phases, by neutron diffraction [3] and computational [4] methods, showed that the order-disorder of Li/Fe distribution plays an essential role in determining the mobility of Li^+ ion in the host framework.
Now the hollandite-type (tetragonal) and orthorhombic (o-$LiMnO_2$-type) polymorphs of $LiFeO_2$ were examined. In particular, the latter phase was shown by electrochemical measurements to actually transform into $LiFe_5O_8$ spinel after few cycles of charge/discharge [2], yet preserving the electrode activity, but with no clear indications of the actual chemical and physical processes therein occurring. First-principles quantum-mechanical simulations (CRYSTAL code, all-electron basis set, hybrid DFT-HF functional) were performed to address two points: (i) the structural changes and energy barriers characterizing the Li^+ ion transfer, and (ii) the actual charge/discharge reactions taking place in the electrode. Several kinds of superstructures and Li^+/vacancy patterns were devised for $Li_{1-x}FeO_2$ ($0 \leq x \leq 0.5$) and $Li_{1+x}Fe_5O_8$ ($0 \leq x \leq 2$), in order to properly account for vacancy formation and ion mobility during the lithium intercatation-deintercalation processes. The corresponding structures were fully relaxed and their energies were calculated, allowing us to determine the electrochemical potentials for a number of possible cathode reactions. As a result, the processes $LiFeO_2 \rightarrow Li_{1-x}FeO_2 + xLi$, $5Li_{1-x}FeO_2 + 5xLi \rightarrow LiFe_5O_8 + 2Li_2O$, and $LiFe_5O_8 + xLi \leftrightarrow Li_{1+x}Fe_5O_8$ are proposed as good candidates to explain the experimental charge/discharge voltage-capacity curves [2]. In the last reaction, both Li and Fe atoms prove to move to octahedral sites on intercalation, changing spinel into a rocksalt superstructure. Thus, the evolution of X-ray powder pattern on cycling is accounted for satisfactorily by simulations based on the least-energy theoretical structures involved in the above series of reactions. Further, pathways of Li^+ ion mobility within the host frameworks are determined, also providing the corresponding activation barriers.

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Titanium Phosphate Hybrid Materials. S. García-Granda. *Physical and Analytical Chemistry Department, University Oviedo, 33006 Oviedo, Spain.*
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Metal salts of phosphoric acid have been known for over a century. In 1964, was obtained the first crystalline such compound, α-$Zr(HPO_4)_2 \cdot H_2O$, which allowed a better understanding of their layered structure and chemical reactivity. Although only two crystalline forms of layered titanium phosphates are known, α-$Ti(HPO_4)_2 \cdot H_2O$ and γ-$Ti(H_2PO_4)(PO_4) \cdot 2H_2O$, many derivatives have been reported, including partially and completely substituted ion-exchanged forms and intercalation compounds. Surprisingly, the γ-layered titanium phosphate is less studied than the α-phase, even though the γ-layers are more rigid, thicker, acidic and amenable to intercalation processes. Now, we revise the structural and thermal data of the γ-titanium phosphate, using

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 ^{1}H 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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Keywords: Phosphate, Hybrid, Titanium

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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 $DyMn_2O_5$ with giant magnetoelectric coupling and two distinct Mn^{3+} and Mn^{4+} 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 Mn^{3+} sublattice, is demonstrated, dismissing a purely electronic mechanism for the multiferroicity.

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Keywords: multiferroics, Friedel pairs, magnetoelectrics.

FA2-MS14B-T02

XRD, XAS and DFT study of the multiferroic mixed-valence compound YMn_2O_5. 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

YMn_2O_5 crystallizes in the structure type of the orthorhombic RMn_2O_5 class of oxides (*R*… rare earth). It shows a series of antiferromagnetic phases where several of them are also ferroelectric. This makes YMn_2O_5 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 $YMn_{2-x}Fe_xO_5$ 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 Fe^{3+} ions occupy the 4*h* Wyckoff site only. Differences of the Mn-XAS spectra with *x* are interpreted in terms of changes of the dipole transitions to 4*p* 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