

M. Meilikhov, K. Yusenko, R.A. Fischer, *Dalton Trans.*, **2010**, 10990. [3] M. Meilikhov, K. Yusenko, A. Torrisi, et al., *Angew. Chem. (Int.Ed.)*, **2010**, 6212.

Keywords: coordination polymers, host-guest complexes, powder structure determination

MS.38.5

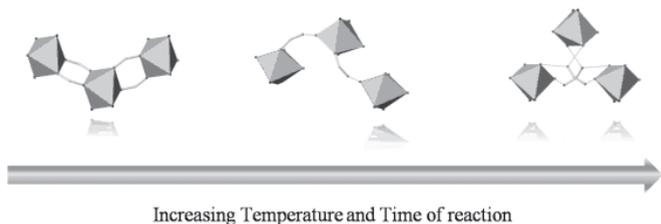
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The role of synthesis conditions on SBU condensation of Mg polymeric frameworks

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Metal-Organic Frameworks (MOFs) represent an extensive group of materials where inorganic secondary building units (SBUs) are interconnected through organic linkers with different functionalities (carboxylates, sulfonates, imidazolates, among others) [1]. Within the applications that have been described for these materials, it is worth highlighting their use in drug delivery, gas/vapour storage/separation and heterogeneous catalysis. In this sense, while the use of transition metals and rare-earth elements is widely known, alkaline-earth metals (AE) have been less considered as suitable coordination centres to obtain new MOFs. However, the advantages that would mean the obtaining of AE MOFs (especially those based on magnesium and calcium [2], [3]) are clear: their low price and the absence of environmental toxicity attributed to these elements.

At present, we are engaged in the obtaining of new Alkaline Earth Polymeric Frameworks (AEPF) based on flexible ligands, which have been yet proved to provoke interesting polymorphism phenomena in MOFs. We present here a peculiar case where the use of a flexible fluoride dicarboxylate ligand (4,4'-hexafluoroisopropylidene) and an additional aromatic nitrogenated ligand (1,10-phenantroline) has given rise to four new phases, for which the inorganic SBUs present different degrees of condensation. Herein, we show the role that play the synthesis conditions on the obtaining of different structural properties, allow us to successfully tackle the synthesis of new AEPFs. Thus, four different Mg-PF materials, which exhibit three- and two- dimensional supramolecular frameworks, were obtained by controlling the synthesis conditions: **i**) a molecular Mg(II) material with polymorphism (AEPF-6, α - and β - phases), **ii**) a 1-D Mg(II) MOF (AEPF-7) and **iii**) a 1-D helical Mg(II) MOF (AEPF-8). A combination of structural and topological comparative analyses with computational studies was performed to depict the structural and energetically processes involved in the synthesis mechanism of these networks.



[1] Metal-Organic Frameworks themed issue, *Chem. Soc. Rev.* **2009**, 38. [2] A.E. Platero Prats, V.A. de la Peña-O'Shea, N. Snejko, A. Monge, E. Gutiérrez-

Puebla, *Chem. Eur. J.* **2010**, 16, 11632 [3] A.E. Platero Prats, V.A. de la Peña-O'Shea, M. Iglesias, N. Snejko, A. Monge, E. Gutiérrez-Puebla, *Chem. Cat. Chem.* **2010**, 2, 147.

Keywords: alkaline-earth metals, topology, theoretical calculations

MS.39.1

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The structure and dynamics of hydrogen storage materials based on boron and nitrogen

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Compounds based on boron, nitrogen and hydrogen are promising candidates for chemical storage of hydrogen. They possess high volumetric and gravimetric storage capacities, and can release hydrogen at relatively low temperatures (less than 200 °C). The crystal structures of these materials are characterised by a high degree of mobility, especially in the positions of hydrogen atoms. The temperature dependence of this mobility results in a number of phase transitions which we have investigated through neutron and X-ray powder diffraction studies, coupled with molecular dynamics simulations and ²H NMR lineshape analysis.

The orthorhombic-tetragonal phase transition of ammonia borane (NH₃BH₃) takes place because of a dynamic reorientation of the NH₃BH₃ molecules about a 4-fold axis at temperatures greater than 225 K. Above ca. 335 K the reorientation becomes more facile and the structure is akin to the "rotator phases" observed for n-alkanes. This high temperature transition is a key step in the thermal release of hydrogen from ammonia borane.

Ammonium borohydride ([NH₄]⁺[BH₄]⁻) has N and B atoms arranged in a rock salt configuration, but the overall symmetry is dictated by the arrangement and dynamics of hydrogen. We have observed a series of phase transitions as ammonium borohydride is cooled and the hydrogen atoms become fixed in a fewer number of positions. Related ionic structures investigated include the diammoniate of diborane ([NH₃BH₂NH₃]⁺[BH₄]⁻) and methylammonium borohydride. The former compound has relatively little hydrogen dynamics, limited to reorientation of the BH₄ groups, but is subtly different from the related chloride. The latter compound exhibits considerable rotational hydrogen disorder and bears a strong resemblance to the analogous halides. X-ray Rietveld refinements of these ionic light element compounds are improved by correct distribution of electron density away from the positively charged amine groups toward the negatively charged borohydride.

Keywords: hydrogen storage, dynamics, phase transitions

MS.39.2

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Synchrotron x-rays and neutrons as essential tools in Li battery research: new structures and new properties of LiFePO₄-based cathodes

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Aqueous routes used for the synthesis of nanoscale particles of LiFePO_4 may lead, under specific conditions, to a full solid solution behavior upon Li^+ extraction at ambient temperature, hence favoring an easier monitoring of the state of charge/discharge of the electrode [1]. We demonstrated through neutron diffraction that this behavior is strongly connected with the presence of significant amounts of structural defects within the crystallites ($\text{Li} \rightleftharpoons \text{Fe}$ exchange, vacancies) [2]. We demonstrated as well that it was possible to monitor and adjust the amount of structural defects through careful annealing in air between 140°C and 500°C , up to a composition close to $\text{LiFe}_{0.67}\text{PO}_4$ [3]. An important feature is that these findings suggest unusually high mobility of Fe within the triphylite framework

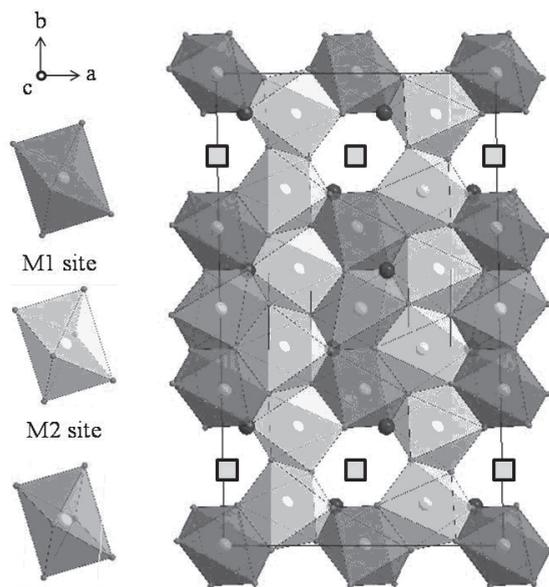


Figure 1: Proposed model for the superstructure of $\text{LiFe}_{23}\text{PO}_4$ built by analogy with the structure of laihunite $\text{Fe}_{2-x}\text{SiO}_4$

The resulting powders show complete new electrochemical features (fig. 1) at various redox steps between 3.5 V and 2.8 V vs Li, associated with partial redistribution of Fe and Li within the octahedral sites, followed by *in situ* Mossbauer spectroscopy and X-ray diffraction. New crystal super-structures [4] with long range ordering of Fe, vacancies and/or Li (fig. 2), determined through electron diffraction and high resolution Synchrotron X-Ray and neutron diffraction will be presented.

[1] F. Mestre-Aizpurua, S. Hamelet, C. Masquelier, R. Palacin, *J. Power Sources* **2010**, 195(19), 6897-6901. [2] P. Gibot, M. Casas-Cabanas, L. Laffont, S. Levasseur, P. Carlach, S. Hamelet, J.-M. Tarascon, C. Masquelier, *Nature Materials* **2008**, 7, 741-747. [3] S. Hamelet, P. Gibot, M. Casas Cabanas, D. Bonnin, C. Grey, J. Cabana, J.B. Leriche, J. Rodriguez Carvajal, M. Courty, S. Levasseur, P. Carlach, M. Van Thournout, J.M. Tarascon, C. Masquelier; *J. Mater. Chem.* **2009**, 19, 3979-3991. [4] S. Hamelet, M. Casas Cabanas, L. Dupont, C. Davoisne, J.M. Tarascon, C. Masquelier, *Chem. Mater.* **2011**, 23, 32-38.

Keywords: battery materials, phosphates, diffraction

MS.39.3

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A new homologous series of oxygen vacancy ordered strontium manganese perovskite

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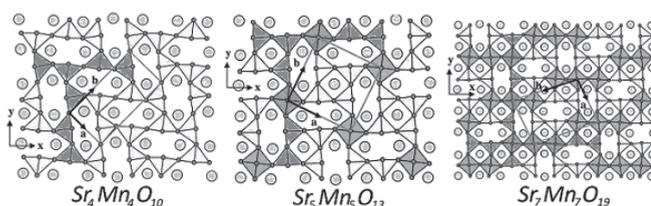
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Perovskite manganites have been extensively studied during last several decades due to a wide range of functional properties like colossal magnetoresistance, mixed ionic-electronic conductivity, and large magnetocaloric effect. Additionally oxygen deficient manganites are relevant as Solid Oxide Fuel Cell cathode materials.

During a systematic study of structural aspects of oxygen deficient $\text{La}_x\text{Sr}_{1-x}\text{MnO}_{3-\delta}$ compounds we determined the structure of a new compound $\text{Sr}_7\text{Mn}_7\text{O}_{19}$ ($\text{SrMnO}_{2.714}$) [1] showing a new oxygen vacancy ordering arrangement. We also found that the previously described vacancy ordered phases $\text{Sr}_2\text{Mn}_2\text{O}_5$ ($\text{SrMnO}_{2.5}$), $\text{Sr}_5\text{Mn}_5\text{O}_{13}$ ($\text{SrMnO}_{2.6}$) and the new phase form a new homologous series of compounds with general formula $\text{Sr}_{4+n}\text{Mn}^{3+}_4\text{Mn}^{4+}_n\text{O}_{10-3n}$ that in certain conditions may accept La substitution [2] and may also be extended to well-known compounds in the $\text{CaMnO}_{3-\delta}$, $\text{LaCuO}_{3-\delta}$ and $\text{NdCuO}_{3-\delta}$ series [3,4,5].

Starting with the $n=0$ member of the series ($\text{Sr}_4\text{Mn}_4\text{O}_{10}$), containing pyramidal Jahn-Teller Mn^{3+} cations, a basic building block for the homologous series is built based on four pyramids lying on the 001 plane with the apex of the pyramids pointing alternatively in the in the [100], [010], [0-10] and [-100] directions in a $p_x p_y p_x p_x$ arrangement. This arrangement repeats in the normal direction of the plane replacing x by y and viceversa. The n^{th} member of the series is built by adding n Mn^{4+} octahedra to the four pyramids keeping the order of the pyramids and the $2/m$ symmetry of the original block. The $n=1$ member $\text{Sr}_5\text{Mn}_5\text{O}_{13}$ is formed with the building block $p_x p_y \text{Op}_y p_x$ while the $n=3$ member $\text{Sr}_7\text{Mn}_7\text{O}_{19}$ is formed by a combination of $p_x p_y \text{OOOp}_y p_x$ and $p_y \text{Op}_x \text{Op}_x \text{Op}_y$ blocks in the x and y direction. The $n=0$ and 1 members of the series are also found in $\text{LaCuO}_{3-\delta}$ and $\text{NdCuO}_{3-\delta}$ systems, while only $n=0$ members are found for $\text{SrCuO}_{3-\delta}$ and $\text{CaMnO}_{3-\delta}$ systems, although many stable compounds with stoichiometries compatible with $n=2$ and 4 have been studied in this latter system.

The lack of observation of $n=2$ and 4 members of the $\text{Sr}_{4+n}\text{Mn}^{3+}_4\text{Mn}^{4+}_n\text{O}_{10-3n}$ series is supposed to be related to the geometrical incompatibility among the two possible $p_x p_y \text{OOOp}_y p_x$ and $p_x \text{Op}_y p_y \text{Op}_x$ building blocks (different from the combination of them in $n=3$ member) and the reduction of stability of structures where two pyramids are linked by the apical oxygen resulting from these blocks. Additionally, A cation size seems to correlate with the lack of observation of other members of the series in the $\text{CaMnO}_{3-\delta}$ system.



[1] L. Suescun et al. *J. Solid State Chem.* **2007**, 180, 1698. [2] L. Suescun et al. *Chem. Mater.* **2008**, 20,1636. [3] A. Reller, et al. *J. Chem. Soc. Chem. Commun.* **1980**, 1378; J. F. Bringley, et al. *Nature (London)*, **1990**, 374, 263; B.-H. Chen, et al. *Inorg. Chem.* **1995**, 34, 2077.

Keywords: homologous_series, manganites, perovskites

MS.39.4

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Polyene-diphenylaniline D5 dyes and their role in the efficiency of DSSC solar cells

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