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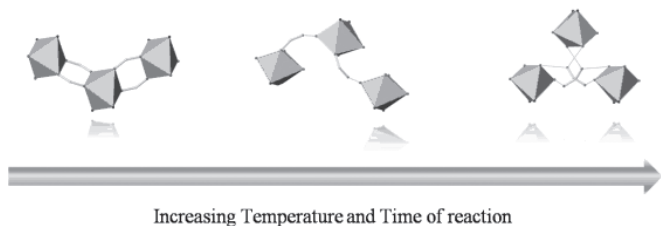
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The role of synthesis conditions on SBU condensation of Mg polymeric frameworks

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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-

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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

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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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