to their extended porosity and chemical and structural versatility.

Recently, we have been using high-pressure to probe these attributes on zeolitic imidazolate framework (ZIF) materials. The first if these to be studied was ZIF-8 ($Zn(MeIM)_2$, MeIM = 2-methylimidazolate) which has a sodalite (zeolitic-type) topology.[1] In this experiment, we surrounded ZIF-8 with a liquid medium (methanol) in the pressure chamber in order to apply pressure evenly, so as not to crush the sample. On application of pressure, we discovered that we could force the medium to enter the pores, causing the sample to *expand*. On increasing pressure further, the framework underwent a phase transition between 0.96 and 1.47 GPa. This transition was driven by the rotation of the methylimidazole rings which dramatically increased both the available pore space and content.

Here, we present a combined experimental and computational approach to understand the behavior of ZIF-8, while presenting new results on the effect of pressure on ZIF-65 ($Zn(NO_2IM)_2$, NO_2IM = 2-nitroimidazolate), to 4.77 GPa which, although topologically similar to ZIF-8, exhibits quite different behavior.

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Keywords: porous, MOFs, high-pressure

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TEM study of pressure-induced C_{60} transformation into ill-ordered graphite phase

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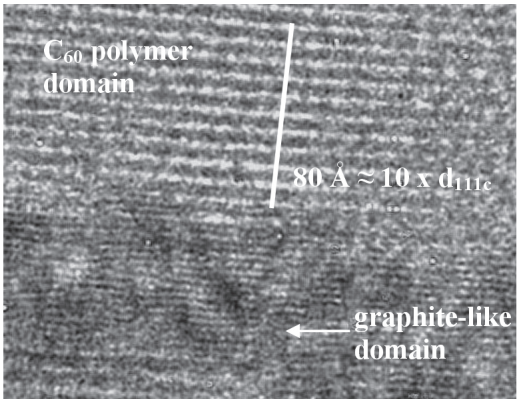
Fullerenes C_{60} have been intensively studied during these last years because of its capacity of creating numerous phases depending on the pressure and temperature conditions during synthesis[1]. The different C_{60} polymers can adopt 1D, 2D or 3D structures in tetragonal, orthorhombic and rhomboedral systems, these structures having been summarized in a reaction phase diagram as reviewed by Moret in 2004,[2]. An interesting point is the transformation of theses phases into ill-ordered "graphite-like" phase above certain values of temperature and pressure[3].

In order to understand the crystallographic relations between polymer and "graphitic" phases, as well as the conformation of the graphite planes on compounds obtained at different pressure conditions, several powder samples have been studied by transmission electron microscopy using electron diffraction (ED) and High Resolution Transmission Electron Microscopy (HRTEM). They were synthesized at more than 1100K in order to achieve the graphite phase transformation under 2 GPa, 5GPa, 8.5 GPa and 10 GPa respectively.

The ED studies for all these samples evidence mostly an ill-ordered graphite-like phase, textured or not, with traces of C_{60} polymer. In order to observe the evolution of interlayer distance between graphite-like planes with pressure, these distances were measured on ED patterns over many particles for each sample. It turns out that it gets shorter with the pressure increase, varying from 3.8 Å at 2 GPa to 3.4Å at 10 GPa. HRTEM imaging displays textured graphite-like undulated planes tangled to each other explaining the texture broadening of the interlayer reflections on ED patterns. On the 5 GPa sample, coexistence of ill-ordered graphite and crystallized C_{60} polymer is observed, both phases getting linked by a pseudo epitaxial relation along the $[111]_c$ direction (c related to cubic, the basic form of C_{60}) of the polymer. This phenomenon was confirmed by HRTEM imaging showing graphite-like domains in a C_{60} polymer matrix (as seen in the figure below).



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High pressure X-ray powder diffraction study of $BaWO_4$

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Barium tungstate ($BaWO_4$) has been shown to be an excellent laser-host material [1] and has been used in the construction of scintillating detectors [2]. In this work we present a study of the structural behavior of $BaWO_4$ under pressure. X-ray diffraction experiments have been carried out up to 20 GPa. Experiments were performed at the HPCAT (16 IDB beamline) using a diamond-anvil cell and under quasi-hydrostatic conditions - neon used as pressure-transmitting medium. Experiments have shown that the tetragonal ($I4_1/a$) structure remains stable up 6 GPa. Upon further compression, phase transitions to lower symmetry structures are detected. The obtained results will be compared with previous results obtained using less hydrostatic pressure media [3, 4] and with *ab initio* calculations [3]. Comparison will be done not only for structural sequences but also for bulk and axial compressibilities. In addition, the effects of pressure in the tetragonal distortion of the low-pressure phase and bond compressibility will be discussed. Rietveld refinements of different structures at several pressures will be also reported.

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Keywords: high_pressure, X-ray_diffraction, phase_transition

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The Effect of High-Pressure on Molecular Magnetism

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Polynuclear clusters of paramagnetic metal ions have attracted intense study since the discovery that such molecules can display the phenomenon of single-molecule magnetism [1]. The energy barrier to the relaxation of the magnetisation implies a large ground state spin multiplicity (*S*) and a significant zero-field splitting (*D*) of that ground state. The strength of coupling and the magnitude of the zero-field splitting are governed by the molecular geometry. Here we show that the application of hydrostatic pressure can significantly change the intra-molecular bond lengths and angles – and in some cases the connectivity - in a host of molecular or molecule-based complexes and in-so-doing greatly modify the observed magnetic parameters [2-7].

Two 'Mn_6' SMMs, hydroxo-bridged Cu dimers and Cu-based chains can all be structurally and magnetically distorted by pressure. We describe the combined high pressure crystallographic and high pressure magnetism and high pressure EPR experiments performed on these materials.

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Structural and related electronic transitions in $GaFeO_3$ under high pressure

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Structural studies of $GaFeO_3$ (SG $Pc2_1n$), an antiferromagnetic (T_N=200 K) *Mott* insulator to 70 GPa, complemented by ^{57}Fe Mössbauer spectroscopy and resistance measurements at compression and decompression reveal a fascinating sequence of structures. Starting at ~ 25 GPa a new structure, an orthorhombic perovskite (*Pbnm*), is sluggishly formed followed by a *V(P)* drop of -5.4%. The complete formation of the perovskite occurs at 42 GPa. In the 0 – 35 GPa range T_N reaches 300 K and *R(P)* decreases by one-order of magnitude, later on, in the 50 - 57 GPa range, the electrical transport activation energy drops from 0.28 to 0.11 eV. At 50 GPa an isostructural transition is detected, characterized by a discontinuous drop of *V(P)* by ~3%. Mössbauer spectra reveal a non-magnetic component coexisting with the magnetic one at ~ 60 GPa. Its abundance increases and above 77 GPa no sign of a magnetic hyperfine interaction is detected down to 5 K. Concurrently, one observes a continuous yet precipitous decrease in *R*(*P*) taking place in the 58-68 GPa range, leading to an onset of the metallic state at P > 68 GPa. These electronic/magnetic features of the high pressure (HP) perovskite are consistent with a *Mott* transition (*MT*).

With pressure decrease, below 52 GPa, the *insulating* perovskite is recovered, and at 23 GPa a 1st-order structural transition takes place to the $LiNbO_3$-type structure with *R3c* SG. This structure remains stable down to ambient pressure and with recompression it is stable up to 50 GPa, afterwards it transforms back to the *HP* perovskite structure. It is noteworthy that this transition occurs at the same pressure, regardless of the preceding structures: *Pbnm* or *R3c*. The results are compared with hematite (Fe_2O_3, SG $R\bar{3}c$) [1, 2] and other ferric oxides. The mechanisms of the transitions are discussed.

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Keywords: high-pressure, phase transitions, mott transition

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Structure and properties predictions for high-pressure crystal structures: BI_3, Mg, and Si

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The recent rich diversity of diffraction studies on crystalline materials at high pressures has provided an opportunity for structural search methods based on first-principles methods to be employed for possible full characterization of structures. In this study, we report on our recent studies using several structure search methods including quasi-random searches, and the metadynamics technique as applied to systems where diffraction data provides a challenge to full characterization of structures. We will focus on several materials where excellent diffraction data has presented additional questions for a full knowledge of several high-pressure crystalline structures. We will use examples including our recent work on BI_3, Mg and Si.

A combination of structure search methods has, for example, been employed to predict the crystalline structure of BI_3 that is agreement with the recently published diffraction data [1]. The use of a combination of methods is demonstrated to reveal the crystalline structure consisting of BI_3 dimers as fundamental components that is most consistent with the diffraction data and reported properties such as phase transition pressures and metallization of this material.

Our investigation of the phase diagram of Mg addresses the question on phase transitions in this material. First-principles metadynamics and density functional methods were employed to investigate the temperature dependence of structural transitions in Mg. The phase identified as a double hexagonal close-packed phase and its location in the phase diagram of Mg at high pressure and temperature is