

Resolution Powder Diffraction beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The study was performed at two different temperatures (750°C and 850°C), during 60 hours under 200 mbar of oxygen. Data analysis was done using Topas program (Bruker AXS).

A complex oxide structure was identified, with five different oxides forming in three steps during the high-temperature oxidation treatment. The phase growing during the first oxidation stages was identified and the time when detrimental oxides appear was measured at both temperatures. In parallel, the quantitative analysis of the in-situ powder diffraction patterns brought information about the reaction kinetics.

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Keywords: low-chromium steel, oxidation, in-situ synchrotron diffraction

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Structural properties of AFeO_{3-δ} perovskites. Effect of A-site parameters

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The structural properties for the AFeO_{3-δ} perovskite materials can be changed using the size and charge of the A sites cations (A = Ln_{1-x}M_x) [1]. The A-size can be evaluated through the mean A-cation radius, $\langle r_A \rangle$, and the size variance or size disorder, $\sigma^2(r_A)$, which describes the mismatch in ionic radii of the cations at the A-site [2].

The AFeO₃ system has been chosen due to the potential properties and stability of these materials as cathodes for Solid Oxide Fuel Cells [3].

This work summarises the independent studies on the separate effects of $x \langle r_A \rangle$ [4] and $\sigma^2(r_A)$ [5] in the structural properties of AFeO₃ perovskites. In order to separate their contribution to the changes in the structural properties, perovskites with general formula Ln_{1-x}M_xFeO_{3-δ} (Ln = La, Pr and/or Nd; M = Sr, Ca and/or Ba) with $0.2 \leq x \leq 0.8$; $1.21 \leq \langle r_A \rangle \leq 1.25 \text{ \AA}$ and $0.0021 \leq \sigma^2(r_A) \leq 0.0155 \text{ \AA}^2$ have been synthesised by conventional ceramic solid state reaction under identical synthetic conditions. The samples have been characterised by X-ray powder and neutron powder diffraction and Rietveld analysis. For each series, one parameter has been varied independently keeping the other two constant.

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Investigations of LiMn₂O₄ nanocrystalline electrode materials

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Lithium manganese oxide (LiMn₂O₄) is a potential candidate for cathode material in Li-ion batteries (LIBs) due to its low cost, low toxicity and high safety. These make LiMn₂O₄ a material promising for use in large scale batteries for powering electric vehicles (EV) or hybrid electric vehicles (HEV) [1]. The high energy density lithium ion batteries need cathode materials with both large volumetric capacity and high density. Nanocrystalline lithium manganese oxide (LiMn₂O₄) material of spinel structure was synthesized by modified sol-gel method using citric acid as a first chelating agent. As the second agent was used glycol ethylene, glycolic acid or acetic acid [2]. The calcination temperature was 450-700°C for a few hours in air. The obtained samples were characterized by the following methods: scanning electron microscopy (SEM/EDX), X-ray photoelectron spectroscopy (XPS), SQUID magnetometry and EPR. Chemical composition, oxidation state of manganese and magnetic properties were examined.

The SEM images show different size of the grains depending on the synthesis process (the example image is shown below). Some contaminations with sodium, potassium or fluor were coming from the starting materials or technological processes. The XPS the complex Mn3p lines were deconvoluted to find the intensity of the Li 1s line and its content in the examined compounds was determined. The ratio of Mn³⁺/Mn⁴⁺ depended on the synthesis process. The C1s lines of the measured samples were intense and complex due to not well-chosen calcination time and temperature. The results were referred to the magnetic measurements results and ESR showing a presence of some extra magnetic phases.

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Keywords: spinel , battery

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Probing 'breathing' mechanisms of ZIFs with high pressure

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Porous materials have attracted a wide scope of interest within the scientific community for a range of possible uses based primarily upon their large surface areas. Metal-organic frameworks (MOFs) are forming an increasingly attractive sub-section of porous materials due

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 of these to be studied was ZIF-8 ($\text{Zn}(\text{MeIM})_2$, 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 ($\text{Zn}(\text{NO}_2\text{IM})_2$, 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

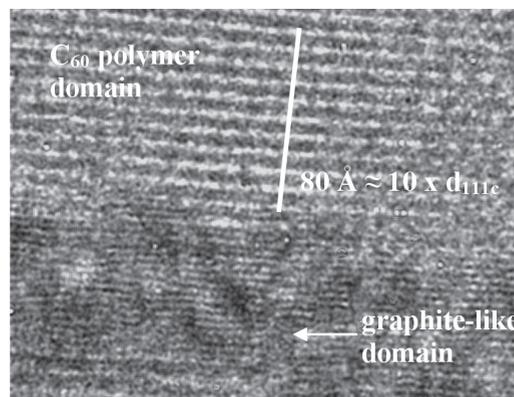
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Fullerenes C_{60} have been intensively studied during these last years because of its capacity of creating numerous phases depending on the pressure and temperature conditions during synthesis[1]. The different C_{60} polymers can adopt 1D, 2D or 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 these 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 BaWO₄

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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 to 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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