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Structural analysis of mechanochemical reaction products from powder diffraction

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Our present research efforts are dedicated to the study of supramolecular reactions between crystalline solids by solid state grinding. This process can offer alternative synthetic routes, occasionally yielding products (structures or stoichiometries) not obtainable from solution chemistry [1]. Moreover, mechanochemical reactions are carried out avoiding the use of crystallization solvents or using minimum quantities of them, e.g. liquid-assisted grinding (LAG) [2], which can afford reduced pollution and economical advantages in large scale syntheses.

The mechanochemical reaction products are always powders. In this work we show the application of direct-space methods for the crystal structure analysis from high-resolution X-ray powder diffraction data, to the solid state characterization of the elusive black polymorph of the charge transfer salt tetrathiafulvalene-chloranil (TTF-CA), obtained by our group as LAG product using water to form a paste with the reactant solids.

The crystal structure of the pseudo-neutral TTF-CA green polymorph (also prepared mechanochemically by LAG with acetone), with charge transferred between TTF and CA molecules of $\rho=0.3e^-$ is known [3], since it is a prototype material [4] for the study of a neutral to ionic transition, accompanied of a crystallographic phase transition with loss of inversion symmetry in the crystal and TTF and CA molecules (from $P2_1/n$ to Pn), at atmospheric pressure and $T\sim 81K$ [3]. The slightly more dense and ionic ($\rho=1e^-$) black form (triclinic, $Z=2$) is the first TTF-tetrahalo-*p*-benzoquinone structure made of $[TTF^+]_2$ and $[CA^-]_2$ dimers, in agreement with the analysis of its FT-IR spectrum [5]. This new packing motif of TTF-tetrahalo-*p*-benzoquinones is interesting because segregated stacks of TTF units with a partial charge transfer between TTF molecules (electron donor) and an electron acceptor are sought for the formation of TTF-based molecular conductors. The material does not show a crystal phase transition between room temperature and 20K.

Moreover, this work is also an example of the ability of the small quantities of solvent used in LAG to direct the formation of a particular polymorph of the products, issue of broader interest such as pharmaceutical cocrystal synthesis by mechanochemistry.

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In-situ XRD study of the reduction of copper spinel with H₂ and CO

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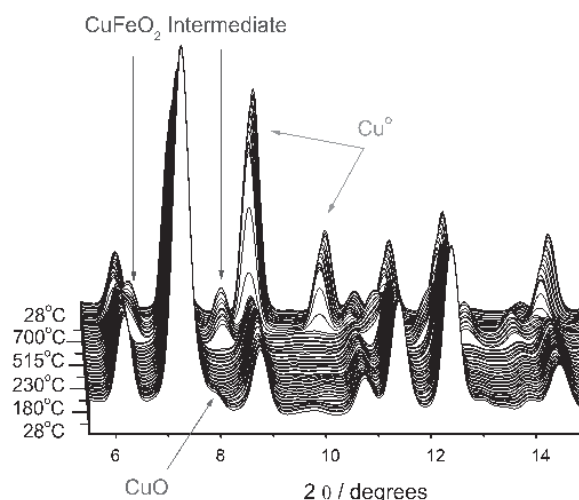
Spinel structured ferrites such as $CuFe_2O_4$ have been used in many industrial and catalytic applications [1]. In particular copper and iron oxides are relevant catalysts for the Water Gas Shift reaction among others [2].

The $CuFe_2O_4$ structure is an inverse spinel structure in which the copper ions occupy the octahedral sites and the iron ions occupy both the tetrahedral and octahedral sites [1]. Along this work we aim to study the temperature programmed reduction process under He, H₂ and CO gas flow conditions, in order to understand the ongoing structural transformations upon interaction with reactants and the thermal stability of the mixed oxide system.

In situ time-resolved X-ray diffraction (TR-XRD) experiments were carried out on beam line X7B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The sample was loaded into a quartz cell of 1 mm diameter, which was attached to a flow system. Two dimensional powder patterns were collected with a Mar345 image plate detector and the powder diffraction rings were integrated using the FIT2D code.

In the Figure we can follow the evolution of the crystallographic phases under a temperature programmed reduction experiment in a 5%CO/He flow. Firstly, with heat some of the segregated CuO is incorporated in the spinel structure. At 180°C the flow is switched to inert He. Around 500 °C, under a plain He flow, the spinel structure is no longer stable and transforms into a Cu^{+1} delafossite $CuFeO_2$ intermediate. Finally, heating to 700 °C triggers the phase segregation into pure magnetite (Fe_3O_4) and metallic copper. Further experiments analyze the reduction under H₂ and also the re-oxidation process.

There is a strong interaction between copper and iron species in this mixed oxide system. Depending on temperature and atmosphere copper species adopt different oxidation states and chemical coordination by incorporating and leaving the spinel structure. This study highlights the importance of *in situ* XRD measurements in order to shed light on the relationship between structural changes and chemical reactivity.



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