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On a new FeOF polymorph: Synthesis and stability

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ABSTRACT

A new polymorph of FeOF (up to now only known in its rutile type structure) was prepared by using a new synthesis approach formally based on anionic exchange using the well-known layered FeOCl as precursor. The synthesis was achieved using $[CH_3C(CH_2O-)_2(COO-)B]$ to vehicle fluorine through the formation of soluble $(CH_3)_4N^+$ $[CH_3C(CH_2O-)_2(COO-)BF]^-$ and using N,N-dimethylformamide (DMF) as the reacting medium. The XRD pattern of layered FeOF can be indexed with an orthorhombic cell which doubles along the *b* axis (which is the direction perpendicular to the layers) with respect to that of pristine FeOCl ($a = 3.792(1)$ Å, $b = 12.699(1)$ Å, $c = 3.321(1)$ Å). Both thermal analysis and diffraction indicate similar stability for the layered and rutile polymorphs. Such findings are rationalized through Density Functional Theory calculations. It is found that the energy difference between the more stable rutile and layered polymorphs is practically nul. The origin of the similar stability lies in the fact that although the number of Fe–F and Fe–O bonds is different in the two structures, the strength of both the total number of Fe–O as well as Fe–F bonds are found to be almost identical. Even if the crystal and electronic structures are considerably different, the total bonding and thus, the stability of the two polymorphs, is comparable. The stability of different FeOF rutile type structures is also analyzed.

1. Introduction

While kinetic control is possible in organic molecular synthesis thanks to reactions taking place at relatively low temperatures and in liquid or gaseous medium, the situation is drastically different in solid state chemistry. Indeed, the traditional approach has relied on the use of high temperature and/or pressure to enable macroscopic diffusion in the solid-state which almost invariably leads to thermodynamic control of the reactions.

Even if the extensive toolbox of chemical reactions available in organic chemistry has no parallelism in solid state chemistry, strategies to deviate from the classical pathways started ca. 40 years ago with the development of *chimie douce* or *soft chemistry* [1]. It is defined as the set of mild chemical operations which allow generating new metastable compounds that have structural filiation between mother and daughter phases [2]. Although metastability and structural relationship are often encountered together, there is no obvious *a priori* connection between both. While reactions taking place at low or medium range temperatures mainly enlist topotactic processes, the obtained phases are not necessarily metastable with respect to polymorphs prepared at higher temperatures using classic solid state reaction protocols. Soft chemistry routes include, amongst others, intercalation/deintercalation processes [3] and ionic exchange on layered phases. There is a single polymorph reported FeOF phase with rutile type structure [4–6], which contrasts to the richer chemistry of other metal oxyfluorides (e.g. five bismuth oxyfluorides are known). Moreover, rutile FeOF is difficult to prepare pure since it requires high reaction temperature and use of sealed containers to bypass the FeF_3 volatility, although alternative methods have been recently proposed [7,8].

In such context, we decided to attempt the preparation of FeOF through a low temperature solution route which might, in principle, yield alternative polymorphs. Since initial attempts of fluorinating Fe_2O_3 in a saturated aqueous NH_4F solution were unsuccessful, we developed a completely different synthesis

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approach formally based on anionic exchange using the well-known layered FeOCl phase as precursor. Several studies were devoted to this compound in the early days of intercalation chemistry and reversible insertion of diverse alkali cations and/or neutral species was achieved [9–12]. Besides, irreversible topotactic reactions involving the formal exchange of Cl^- by OH^-, NH_2^- or anions derived from organic molecules possessing one or two nucleophilic groups were also demonstrated [13–20]. In light of such achievements, the possibility of preparing a layered FeOF polymorph and the study of its relative stability versus the rutile form was attractive. The F^- ion is however a very poor nucleophile in water, and the insolubility of many halides in organic solvents led us to consider a novel route to solubilize a F^- complex while keeping a nucleophilic character.

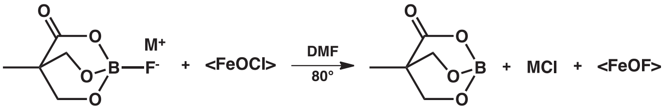
For reasons of clarity the paper will be organized as follows: the synthesis of layered FeOF via the design of novel boron complexes to vehicle F^- species and trigger exchange reactions will be first described and then the stability of both polymorphs will be addressed through DFT calculations and also investigated experimentally through thermal analysis and *in situ* X-ray diffraction with temperature.

2. Experimental

2.1. Synthesis

Rutile FeOF was prepared from a mixture of FeF_3 (Aldrich, 98%) and Fe_2O_3 (obtained by the decomposition of the iron (II) oxalate in air at 400 °C for 10 h) in 1:1 molar ratio (200 mg) placed inside a platinum tube sealed under argon and heated at 980 °C for 24 h and further quenched to room temperature. No reaction was found to occur below 900 °C while treatments at higher temperatures yielded rutile FeOF.

The synthesis of layered FeOF enlists two steps. The first one deals with the preparation of FeOCl via a process derived from Sagua et al. [21] It consists of heating at 350 °C for 48 h a mixture of $FeCl_3$ (Aldrich, 97%) and Fe_2O_3 in 1:1 molar ratio inside a quartz tube sealed under vacuum. The XRD pattern of the recovered powder, made of well crystallized micrometrics particles, was identical to that reported in the literature for FeOCl with similar lattice parameters ($a = 3.7743(1)$ Å, $b = 7.9112(1)$ Å, $c = 3.3017(1)$ Å, *Pmnm* space group). This powder was used afterwards as precursor for conducting an anion exchange reaction which requires the judicious choice of solvents and salts. To prevent the possibility of F^-/OH^- exchange, we decided to use a thermally stable aprotic organic solvent such as anhydrous N,N-dimethylformamide (DMF) as the reacting medium. Lastly, a selective F^- carrier was used, a boron ester with exposed empty sp^3 orbital binding to the fluoride ion and inducing solubility of the salt, without loss of nucleophilicity. Thus, attempts to prepare layered FeOF from FeOCl were done according to the following reaction:



The reaction was carried out under argon atmosphere in a ca. 20 ml of anhydrous DMF (Aldrich, 99.8%) with 1 g of anhydrous tetramethylammonium fluoride $(CH_3)_4NF$ (Aldrich, 97%) as fluorine source and 1 g of $[CH_3C(CH_2O-)_2(COO-)B]$ to vehicle fluorine through the formation of soluble $(CH_3)_4N^+$ $[CH_3C(CH_2O-)_2(COO-)BF]^-$ from 2,2-bis(hydroxymethyl propanoic acid and $B(OH)_3$) and 0.5 g of FeOCl precursor. The suspension was heated at 80 °C for 48 h and a change in color was gradually observed from brown-red FeOCl to black. The resulting solid was recovered by centrifugation, washed with anhydrous methyl formate (Aldrich, 99%) and dried under vacuum at 100 °C overnight prior to be characterized by XRD.

2.2. X-ray diffraction

The X-ray powder diffraction (XRD) patterns were recorded using either a Scintag or a Bruker D8 Diffractometer equipped with a Lindsey counter, both using Cu Kα radiation. The temperature structural evolution was followed by *in situ* XRD using Siemens D8 diffractometer (CoKα = 1.79026 Å) equipped with a position-sensitive detector. Cell parameters were refined from Le Bail fits with the FullProf program [22].

2.3. Microscopy

SEM images were recorded with an FEI Quanta 200F operating at 20 kV in low vacuum, on powders covered with a very thin layer of gold by metal pulverization. TEM pictures were obtained using an FEI Tecnai F20 S-Twin electron microscope operating at 200 kV and fitted with an EDAX EDS. A droplet of a dispersion containing the sample was deposited on a TEM holey carbon copper grid. The measurements to determine the sample elemental compositions were typically carried out on at least 10 different crystals to ensure representativity.

2.4. Thermogravimetric analysis

TGA measurements were carried out between 30 and 800 °C in a constant flow of argon at a rate of 5 °C/min using thermal analyzer STA 449C Jupiter from Netzsch. Differential Scanning Calorimetry (DSC) experiments were carried out on a Netzsch DSC 204F1 heat flux differential calorimeter at a heating rate of 2 °C/min under a constant argon flow of 200 mL/min. The calibration was performed with gallium, KNO_3, indium, tin and bismuth references. Afterward, the samples were placed in aluminum pans covered with a pierced lid. Unless specified, the samples were heated from 30 °C up to 600 °C.

2.5. DFT calculations

First-principles spin-polarized calculations were carried out using a numerical atomic orbitals DFT approach [23,24] developed for efficient calculations in large systems and implemented in the SIESTA code [25–27]. We have used the generalized gradient approximation (GGA) to DFT and, in particular, the functional of Perdew, Burke and Ernzerhof [28]. An on-site Coulomb energy (U) correction has been taken into account within the rotationally invariant DFT + U approach of Dudarev et al. [29] Test calculations with different U values were carried out and a value of 6 eV was chosen. Calculations for the rutile structure were carried out using a $2 \times 2 \times 2$ supercell. Only the valence electrons are considered in the calculation, with the core being replaced by norm-conserving scalar relativistic pseudopotentials [30] factorized in the Kleinman-Bylander form [31]. We have used a split-valence double-ζ basis set including polarization orbitals for all atoms [32]. The energy cutoff of the real space integration mesh was 1000 and 800 Ry for the rutile supercell and layered phase calculations, respectively. The Brillouin zone was sampled using grids of $(4 \times 4 \times 6)$ and of $(5 \times 8 \times 16)$ *k*-points for the rutile supercell and the layered phase calculations, respectively [33].