



Influence of temperature and high pressure on the structural and physical properties in **Fe**-based **C**harge **O**rders systems

Note: The results from this document can be cited only after the publication



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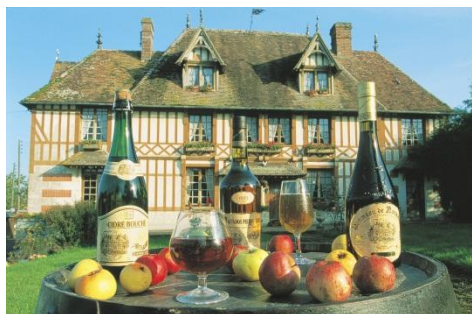
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Partners



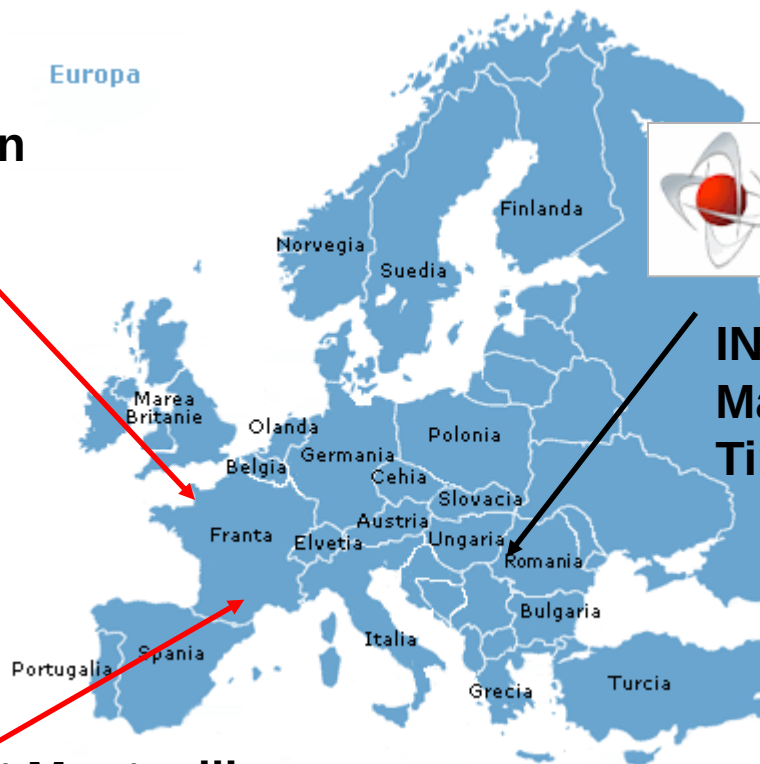
Laboratoire Crismat Caen



Institut Charles Gerhardt Montpellier



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**INCD Electrochimie si
Materie Condensata
Timisoara**



Mixed valent iron oxides

Fe/P/O

Fe/B/O

Fe/As/O

The **main goals** of this collaboration work are:

- **the identification of new multifunctional materials** suitable for applications;
- the consideration of the importance of **adequate synthesis methods**: classic but also unconventional, relatively easy to achieve;
- the establishment of **structures-properties relationships** in mixed valence iron oxides in an extended temperature and pressure range;
- the understanding of **charge ordering in iron oxides** with complex crystal structures and its “stability” vs. temperature and vs. high pressure;
- to understand **the relationship between charge ordering states and exciting physical properties** (for instance, multiferroicity).

Mixed valent iron oxides

Fe/P/O

Fe/B/O

Fe/As/O

As it was written in our project proposal, the first year (2013) is dedicated to the preparation of samples in the 3 systems.



The work has been done separately in the 3 laboratories.

A tight collaboration between the involved teams has been accomplished (two project meetings, discussion by emails) and a concerted way for the samples preliminary characterisations (exchange of samples, complementary techniques and of researchers competences).

Synthesis Techniques

Single crystals

- Image furnace
- Hydrothermal
- Flux method

Powder Solid state reaction

Annealing in controlled atmosphere

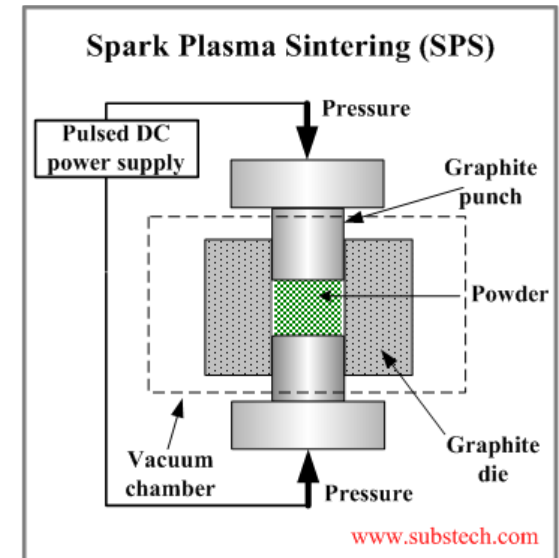
'un-conventional' methods

Hydrothermal synthesis at high temperature and pressure

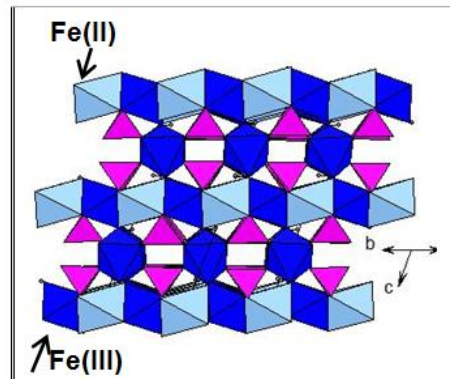
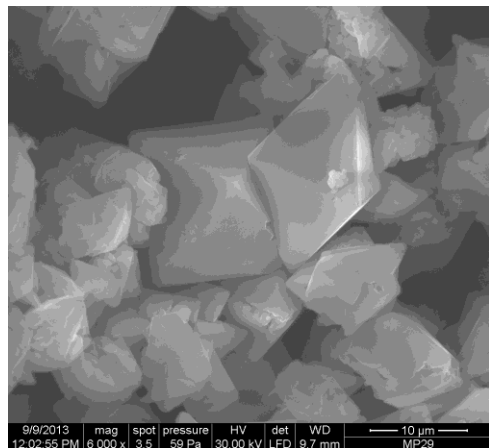


- 1 Monel Alloy 400
- 2 Industrial Pressure Transmitter for High Pressure
- 3 Plug-on Display self powered; P=0-1600 bar

Spark Plasma Sintering (SPS)



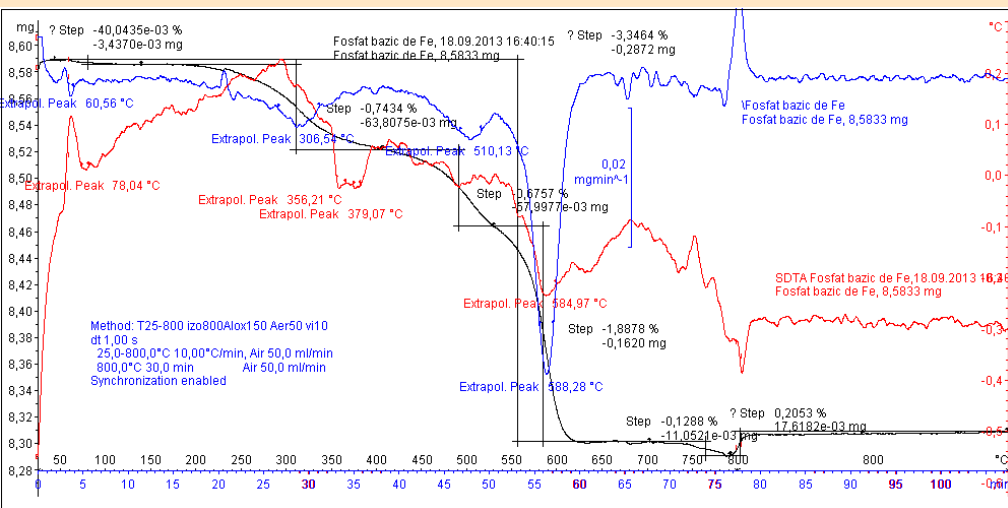
Barbosalite $\text{Fe}_3(\text{PO}_4)_2(\text{OH})_2$



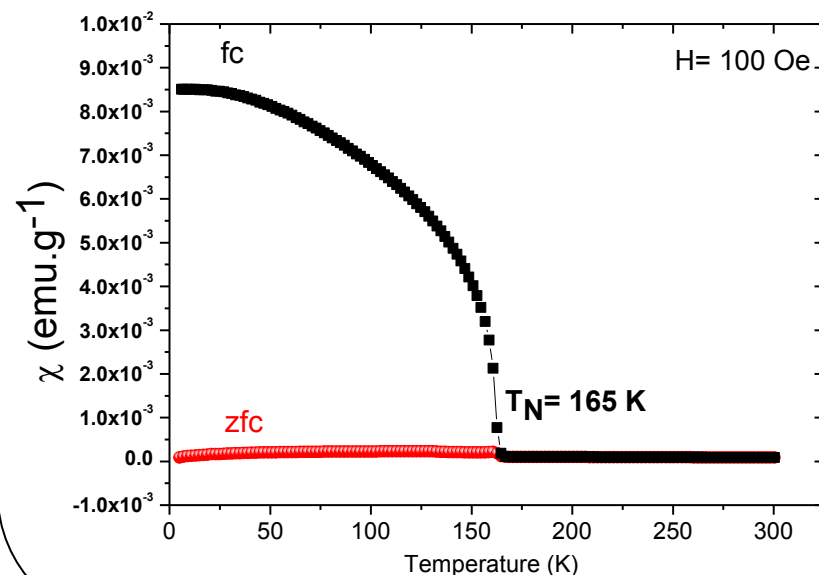
- Space group: $P 2_1/n$
- a (Å): 7,3294
- b (Å): 7,4921
- c (Å): 7,4148
- Alpha (°): 90,000
- Beta (°): 118,433
- Gamma (°): 90,000

G. J. Redhammer et al. Phys Chem Minerals (2000) 27: 419-429

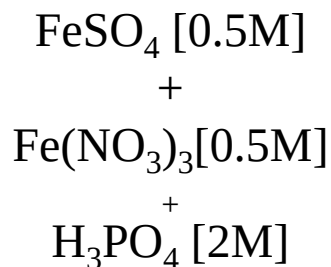
The thermogravimetric analysis : three weight losses at $\sim 70^\circ\text{C}$, 308°C si 588°C , which are attributed to water departure.



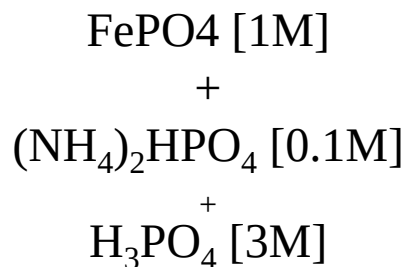
Susceptibility measurements indicate a magnetic transition at $T \sim 165 \text{ K}$.



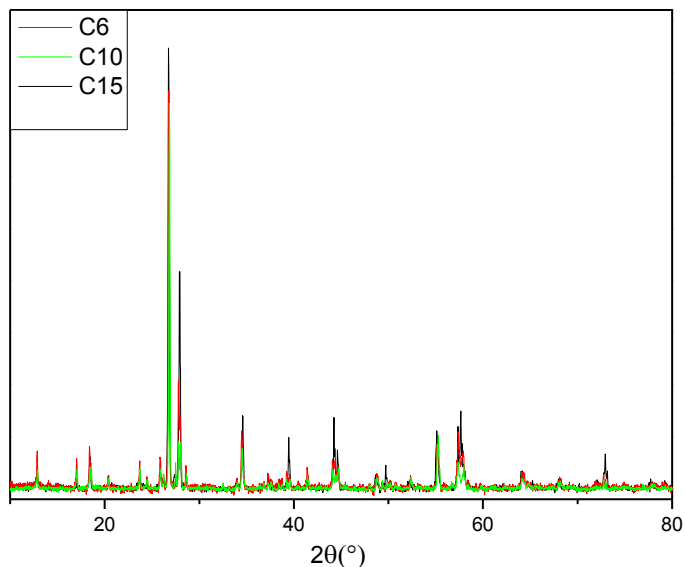
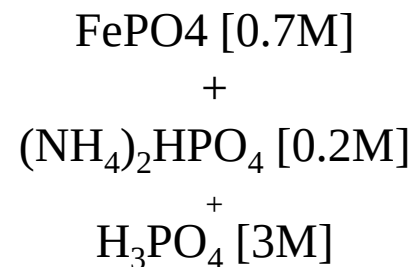
Exp C6 Phosphate



Exp C10 Phosphate



Exp C15 Phosphate



Crystal system: Monoclinic

Space group: C2/c

a (Å): 19.5550

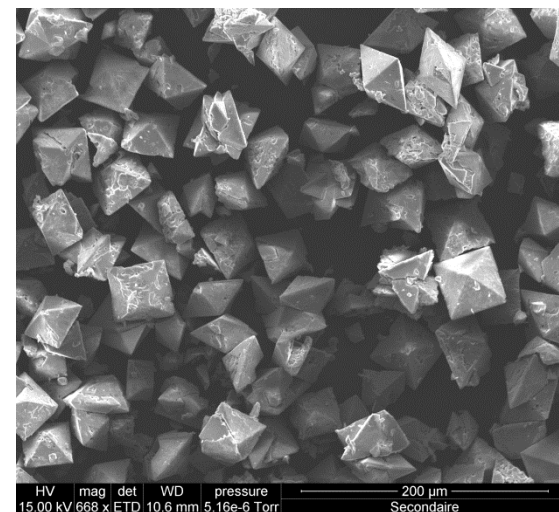
b (Å): 7.3760

c (Å): 7.4290

Alpha (°): 90.0000

Beta (°): 102.2600

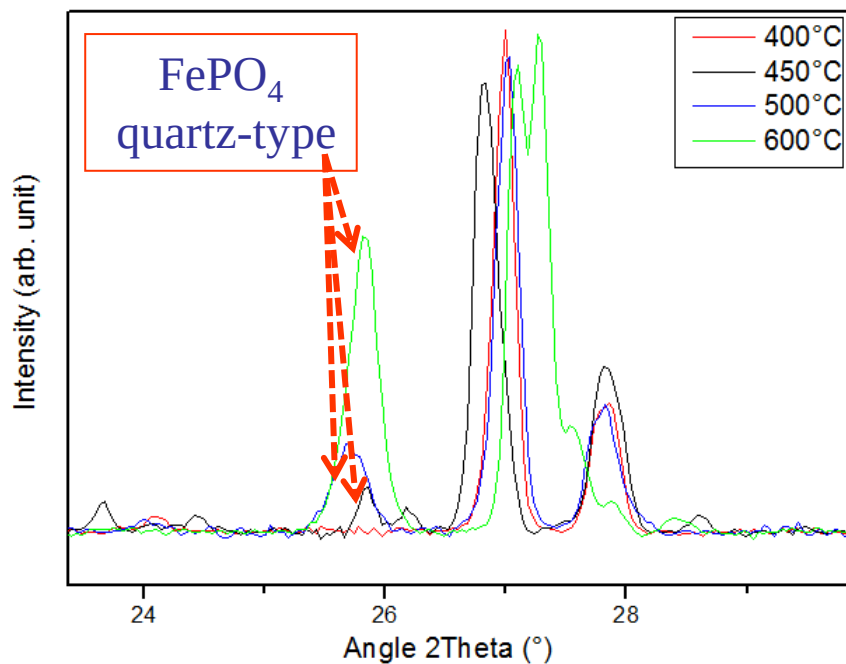
Gamma (°): 90.0000



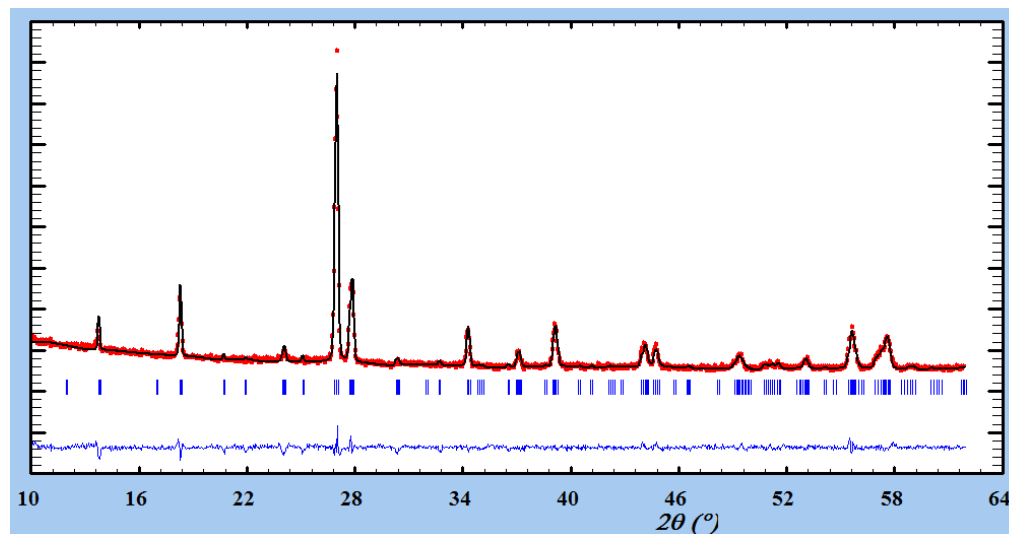
$\text{Fe}_4(\text{OH})_3(\text{PO}_4)_3$

Treatment of $\text{Fe}_4(\text{OH})_3(\text{PO}_4)_3$ under CO/CO_2 atmosphere.

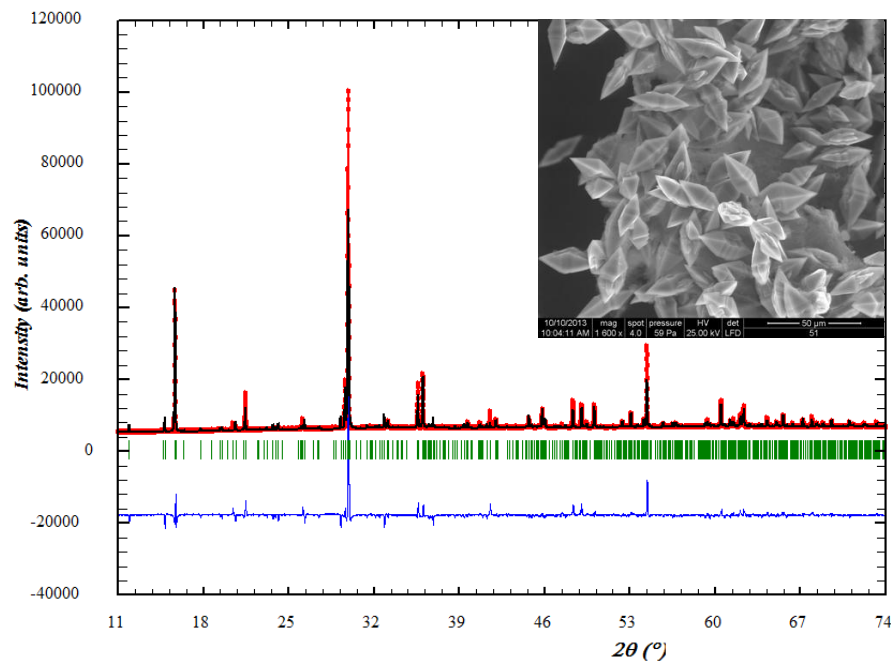
The $\alpha\text{-Fe}_2\text{PO}_5$ phase is obtained at 400°C. Above a FePO_4 phase appears



Lebail fit of $\alpha\text{-Fe}_2\text{PO}_5$



$\text{NH}_4\text{Fe}_2(\text{PO}_4)_2$



$\alpha\text{-NH}_4\text{Fe}_2(\text{PO}_4)_2$

Space group C2/c

$a=19.9225(5)\text{\AA}$

$b=14.8426(3)\text{\AA}$

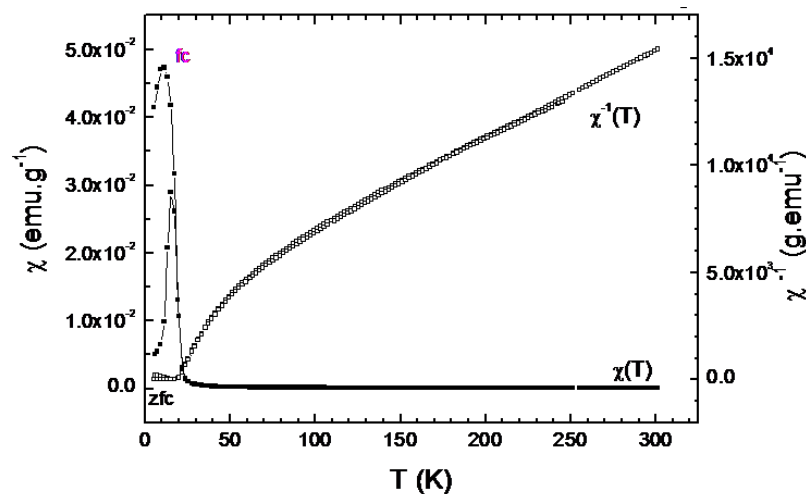
$c=9.9645(2)\text{\AA}$

$\beta=119.2795(7)^{\circ}$

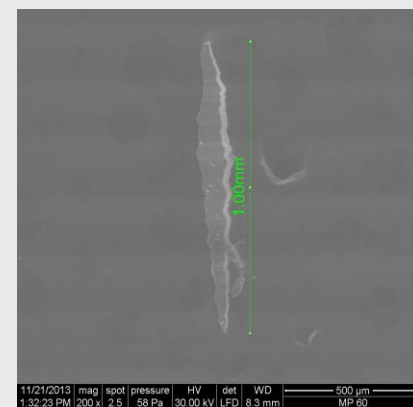
Vol: $2570.110(1)\text{\AA}^3$

FT-IR: NH_4^+ cations: a large absorption band at $\sim 3000\text{cm}^{-1}$ and a narrow one at 1418cm^{-1} .

Susceptibility measurements indicate a magnetic transition at $T\sim 20\text{ K}$.



$\beta\text{-NH}_4\text{Fe}_2(\text{PO}_4)_2$

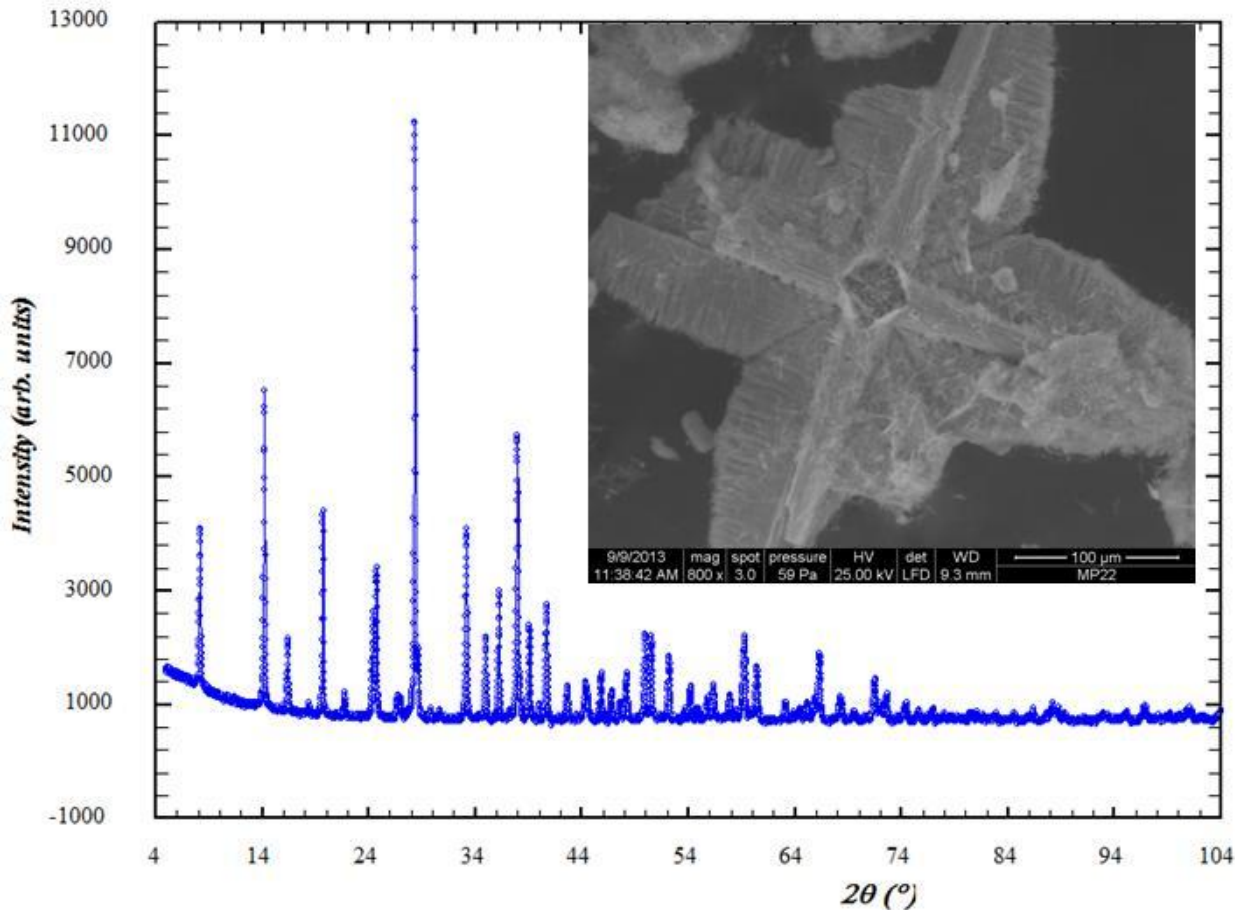


New material Ni/Fe/P

Hydrothermal synthesis

$1\text{M FePO}_4 + 1\text{M Fe(NO}_3)_3 \times 9\text{H}_2\text{O} + 2\text{M H}_3\text{PO}_4$

$T=310\text{ C, }P=800\text{ bars}$



EDS

Elem	Wt %	At %	K-Ratio
AlK	1.01	1.23	0.0024
P K	15.49	16.33	0.0660
FeK	24.74	14.46	0.2560
NiK	34.99	19.46	0.3139

Susceptibility measurements indicate a magnetic transition at $T_N \sim 67\text{ K}$.

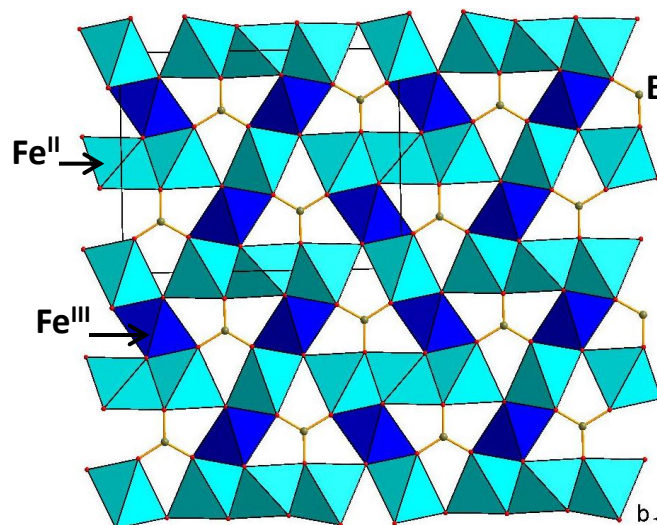
Mixed valent iron borates : the studied materials

• Fe_3BO_5 (*ludwigite*) [1]

Orthorhombic $P b m a$

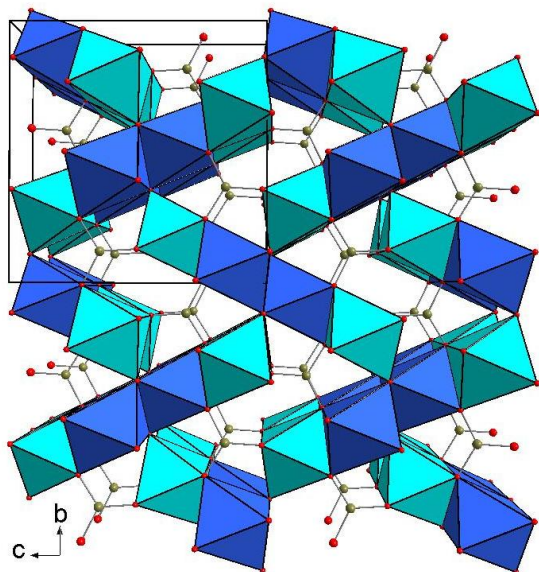
$a = 9.458 \text{ \AA}$, $b = 12.304 \text{ \AA}$, $c = 3.078 \text{ \AA}$

Edge-sharing FeO_6 octaetra forming infinite chains, connected through the corners of their polyedra and through BO_3 groups.



Projection of the structure of Fe_3BO_5 along [001]

• Fe_2BO_4 (*warwickite*) [2]



Projection of the structure of Fe_2BO_4 along [100]

Monoclinique $P2_1/c$

$a = 3.1688 \text{ \AA}$, $b = 9.3835 \text{ \AA}$, $c = 9.2503 \text{ \AA}$

$\beta = 90.22^\circ$

Ribbons formed by four edge-sharing FeO_6 octaetra, connected through the corners of their polyedra and through BO_3 groups.

[1] M. Mir et al, *J. Appl. Crystallogr.* 39 (2006) 39-42

[2] A.M.T. Bell et al., *Mater. Sci. Forum* 278 (1998) 708-713

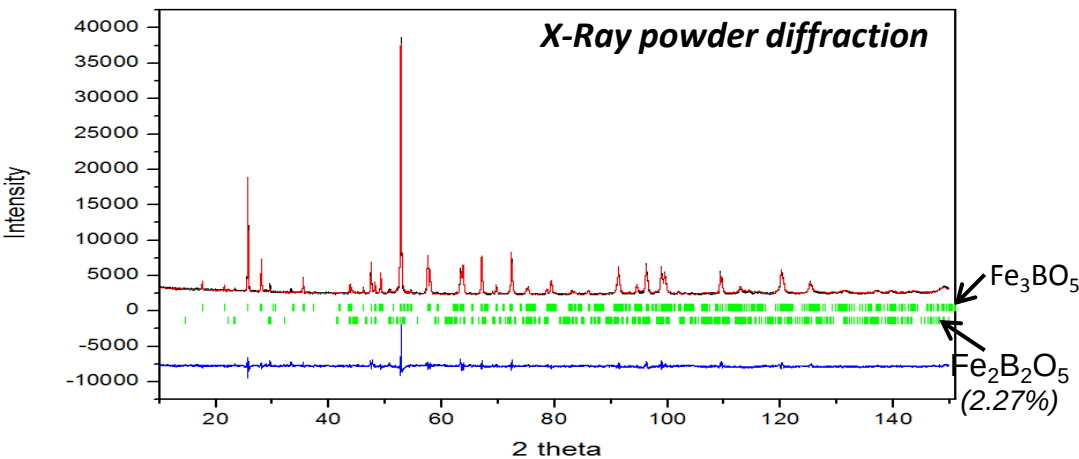
Mixed valent iron borates : first results

- Fe_3BO_5 (*ludwigite*)

Precursors : Fe_3O_4 , Fe, B_2O_3

1) Synthesis at 820°C in an evacuated silica ampoule $\rightarrow \text{Fe}_3\text{BO}_5 + \text{Fe}_3\text{O}_4$

2) Annealed four times + B_2O_3 at $820^\circ\text{C} - 120\text{h} \rightarrow \text{Fe}_3\text{BO}_5$ (+ $\varepsilon\text{Fe}_2\text{B}_2\text{O}_5$)



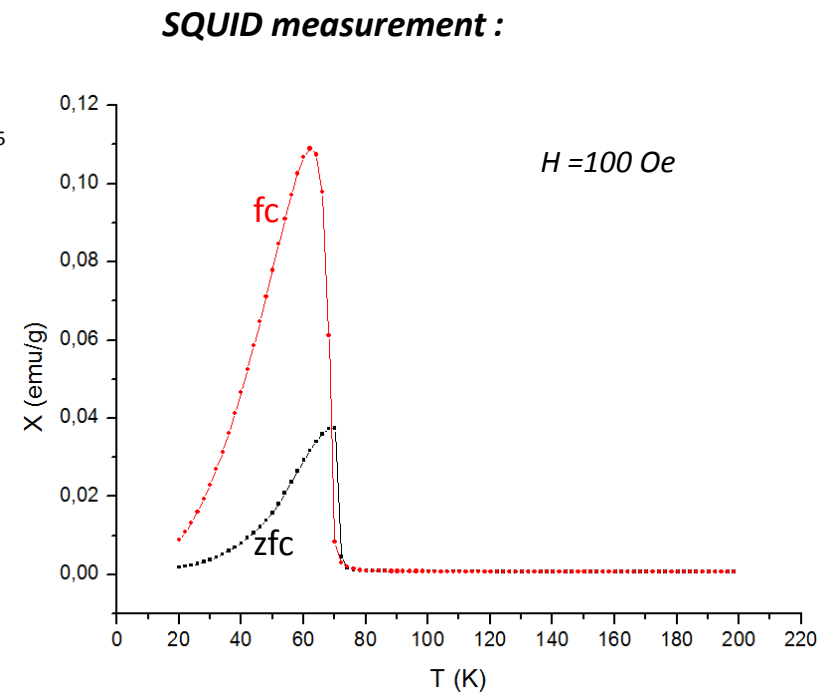
Le Bail fit :

Orthorhombic P b n m

$a = 9.4600 \text{ \AA}$,

$b = 12.3112 \text{ \AA}$,

$c = 6.1522 \text{ \AA}$



Mixed valent iron borates : first results

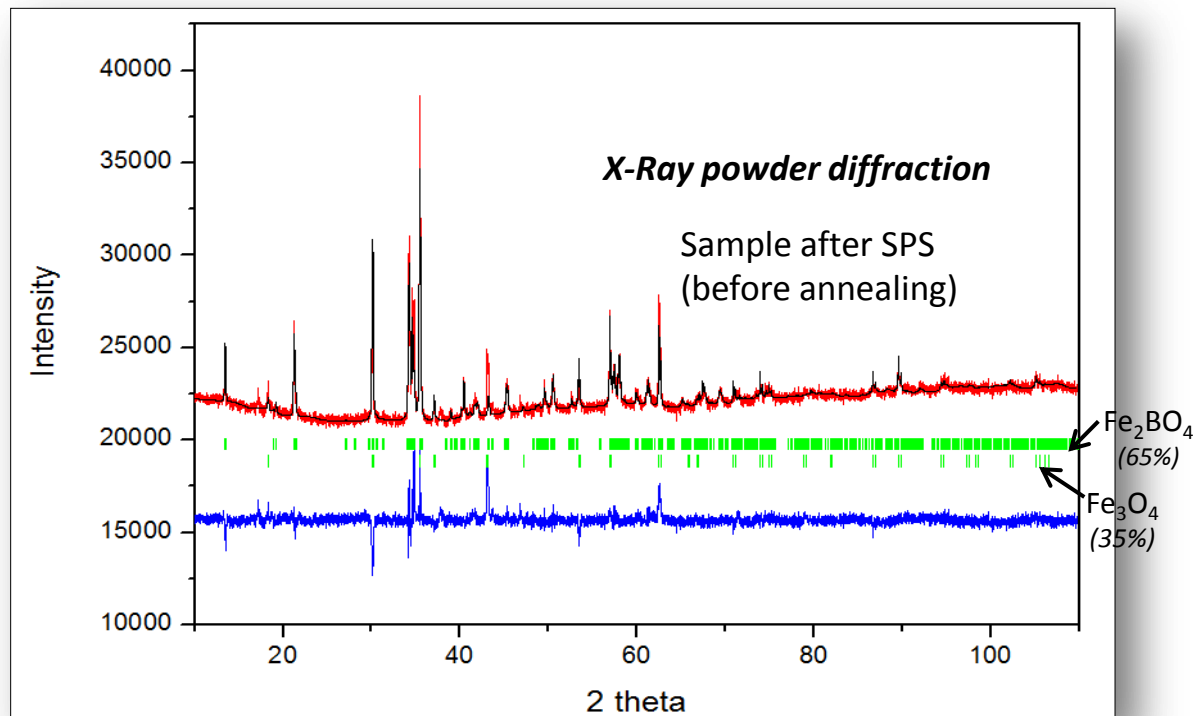
- Fe_2BO_4 (*warwickite*)

Precursors : Fe_3O_4 , Fe, B_2O_3

1) Spark Plasma Sintering (SPS) : 51MPa, $\Phi=15\text{mm}$, 900°C , $t=6\text{h}$

→ 65% Fe_2BO_4 + 35% Fe_3O_4

2) Annealed + 10% B_2O_3 at 900°C – 60h → 99% Fe_2BO_4 + 1% Fe_3O_4



Conclusions - 2013

Mixed valent iron oxides

Fe/P/O	Fe/B/O	Fe/As/O
$\text{Fe}_3(\text{PO}_4)_2(\text{OH})_2$	Fe_3BO_5	In progress..
$\text{Fe}_4(\text{OH})_3(\text{PO}_4)_3$	Fe_2BO_4	
$\alpha\text{-Fe}_2\text{PO}_5$		
$\text{NH}_4\text{Fe}_2(\text{PO}_4)_2$		

New material Ni/Fe/P

➔ Success in the preparation of mixed valent iron oxides : Fe/P/O and Fe/B/O !!

- Next year :
- Synchrotron X-Ray diffraction, neutron diffraction, TEM;
 - studies in function of T, H and P ;
 - next meeting planed for spring in Timisoara, Romania.

To be continued....