

High pressure synthesis, structure, physical properties of Pb(V,A)O₃, A = Fe, Ti

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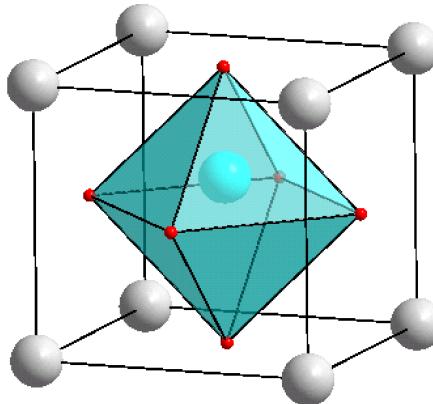
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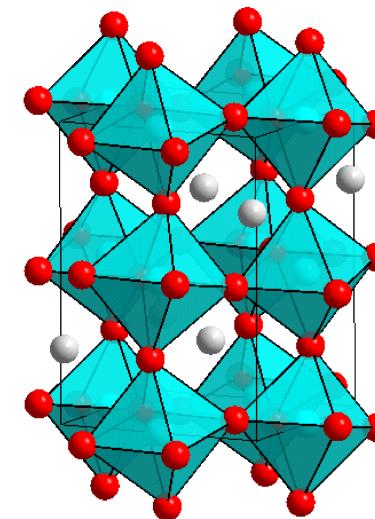
Introduction

Perovskite compounds ABO_3

Ferroelectricity and magnetic ordering mutually exclusive



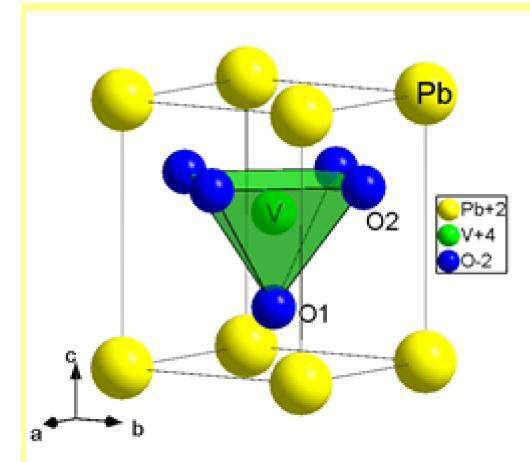
Ferroelectric perovskites
Isolants, lone pair + 3d0
NON-
CENTROSYMETRIC



Magnetic Perovskites
3dn, (Jahn Teller, tilts...)
CENTROSYMETRIC

Introduction

PbVO₃ appears as an interesting candidate:
isostructural to the ferroelectric PbTiO₃
cations V⁴⁺ spin $\frac{1}{2}$



Some results and questions :

Structure

S.G. $P4mm$ $a = 3.80005(6)$ Å, $c = 4.6703(1)$ Å,
the largest tetragonal distortion, $c/a = 1.23$, among the PbTiO₃
compounds

Shpanchenko, R. V et al. C. Chem. Mater. 2004, 16, 3267–3273

Introduction

Magnetism: not so clear...

Long-range ordering or short range ordering?

NPD: neither extra antiferromagnetic peaks nor an increase in the nuclear Bragg peaks were observed at the temperature $T = 1.5$ K
(pb impurities PbV₆O₁₁)

The magnetic susceptibility of polycrystalline samples of PbVO₃ + single crystal: two-dimensional S=1/2 square lattice antiferromagnet with long range order at TN = 43 K (μ Sr) = 50K (M=(H))

Due to the electronic configuration of the V⁴⁺ (3d1), which promotes the VO vanadyl bonding with a dxy orbital ordering ?

Magnetic frustration?

Oka, K et al Inorg. Chem. 2008, 47, 7355.

Introduction

Multiferroic: bulk vs thin films...

Experimental measurements of bulk samples and epitaxial thin films show great contrast between each other.

Polycrystal semiconducting samples do not exhibit obvious magnetic transition, while high quality epitaxial thin films show a magnetic transition around 100 K.

Ferroelectricity, proved in thin films with an effective piezoelectric coefficient $d_{33} \approx 3.1 \text{ pC/N}$

Kumar, A et al . Phys. Rev. B 2007, 75, 060101.

Our study

Powder synthesis

Substitution of V by Ti : evolution of the magnetic properties

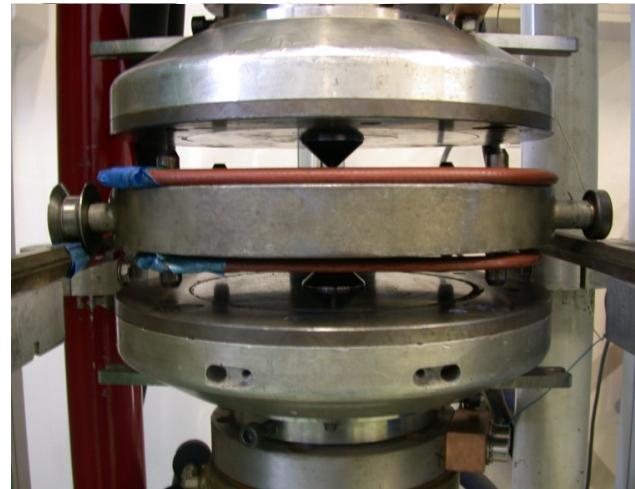
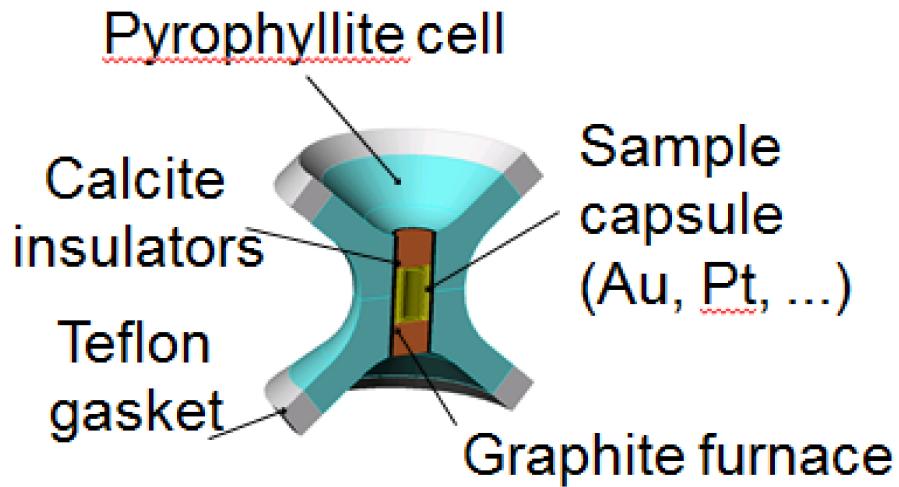
Substitution of V by Fe : new magnetic properties,
new phases ?

Single crystals synthesis

PbVO₃ can only be synthesized at high pressure .

The High pressure – High temperature equipments at the Institut Néel

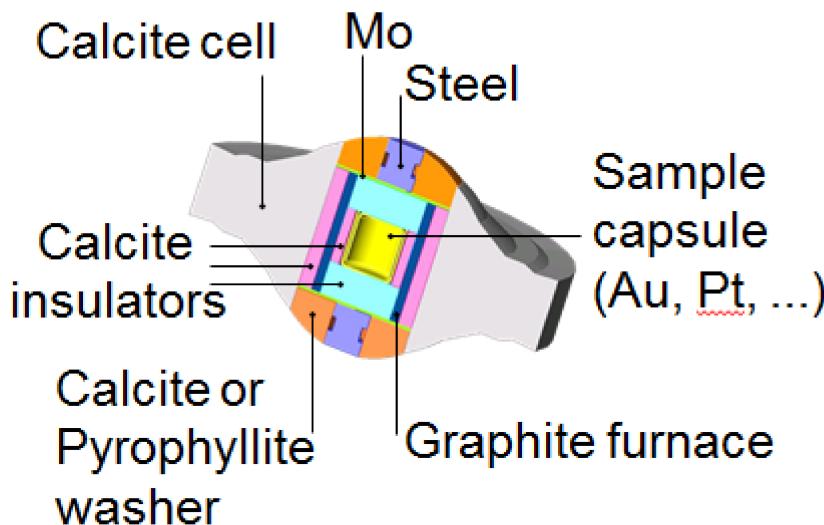
BELT



- 8 GPa, 1500 °C
- Volume : 0.04 cm³

The High pressure – High temperature equipments at the Institut Néel

CONAC



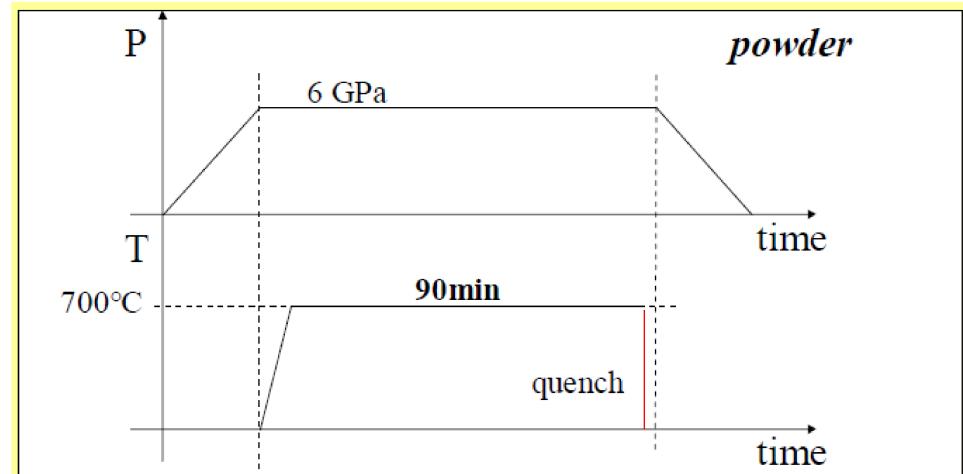
The Conac 40 anvil

CONAC28
 - 7,5 GPa, 1500 °C
 - Volume : 0.17 cm³

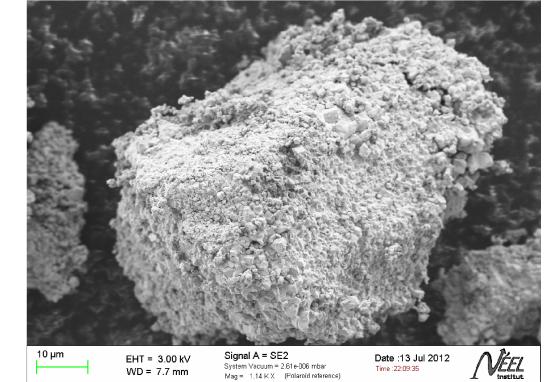
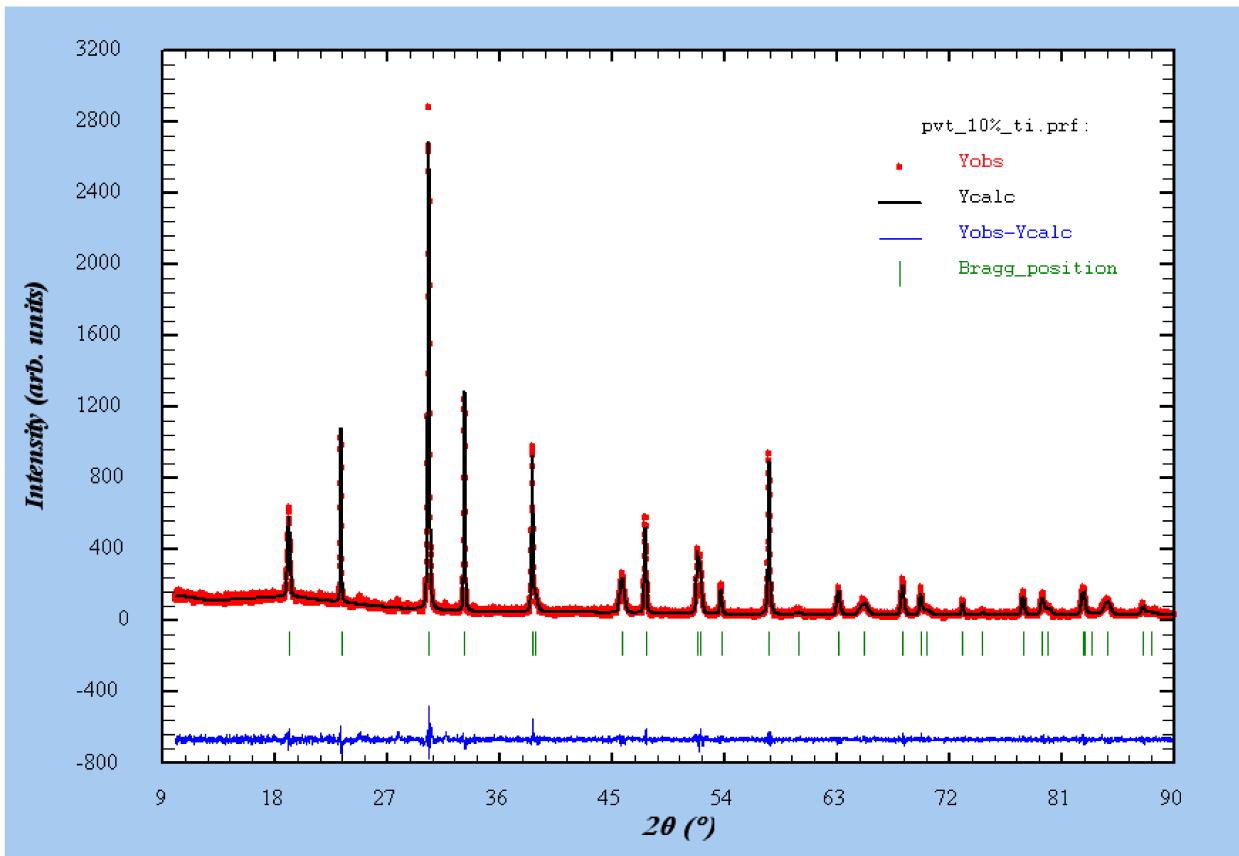
CONAC40
 - 6 GPa, 1500 °C
 - Volume : 0.80 cm³

- Samples were prepared from stoichiometric mixtures of PbO, V₂O₃, V₂O₅, TiO₂ and Fe₂O₃.

Typical pressure and temperature are 6 GPa-700°C.



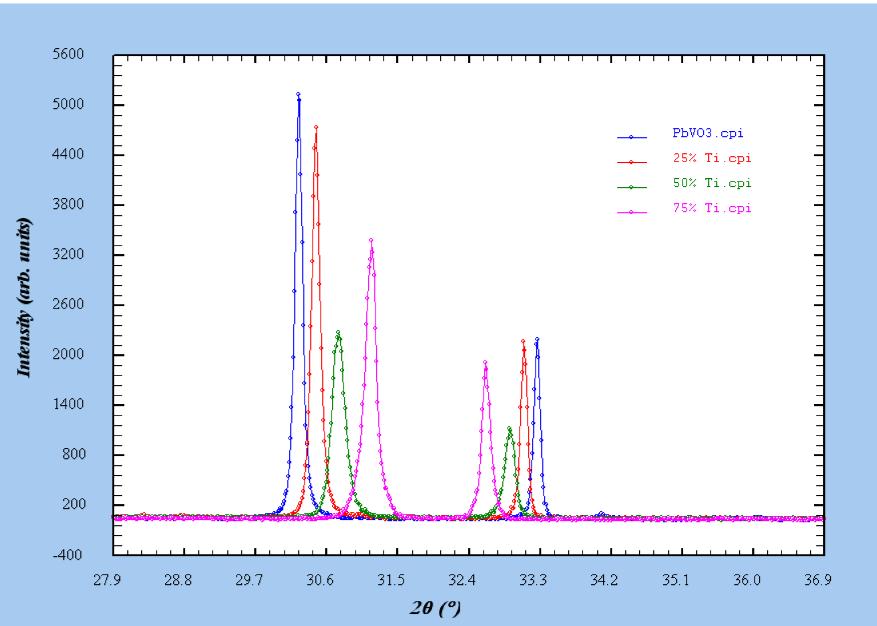
- substitution series (nominal composition)
 - PbV_{1-x}TixO₃ x = 0, 0.1, 0.25, 0.5, 0.6, 0.75, 0.8, 1
 - PbV_{1-x}FexO₃ x = 0, 0.1, 0.25, 0.3, 0.4, 0.5, 0.6, 0.65, 0.75



SEM Image
 $\text{PbV}_{0.6}\text{Fe}_{0.4}\text{O}_3$

Rietveld on PXRD $\text{PbV}_{0.9}\text{Ti}_{0.1}\text{O}_3$
 Almost single phase powder samples were obtained at 6 GPa, 700° C for 90 min dwell time.

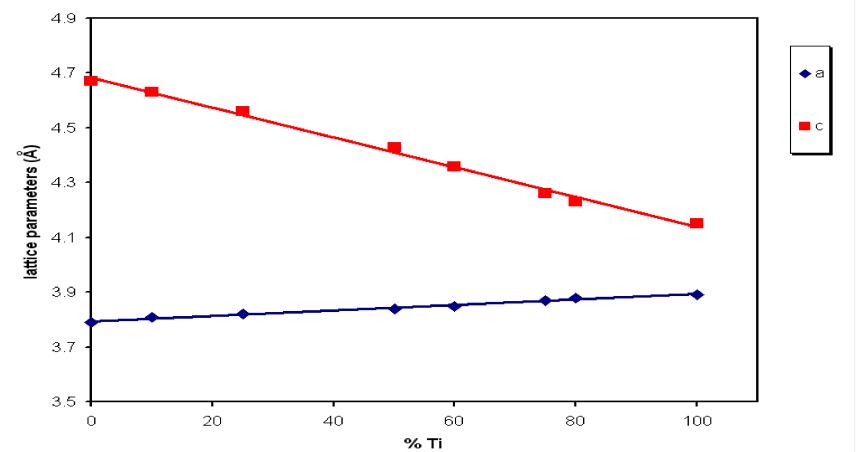
$Pb(V_{1-x}Ti_x)O_3$



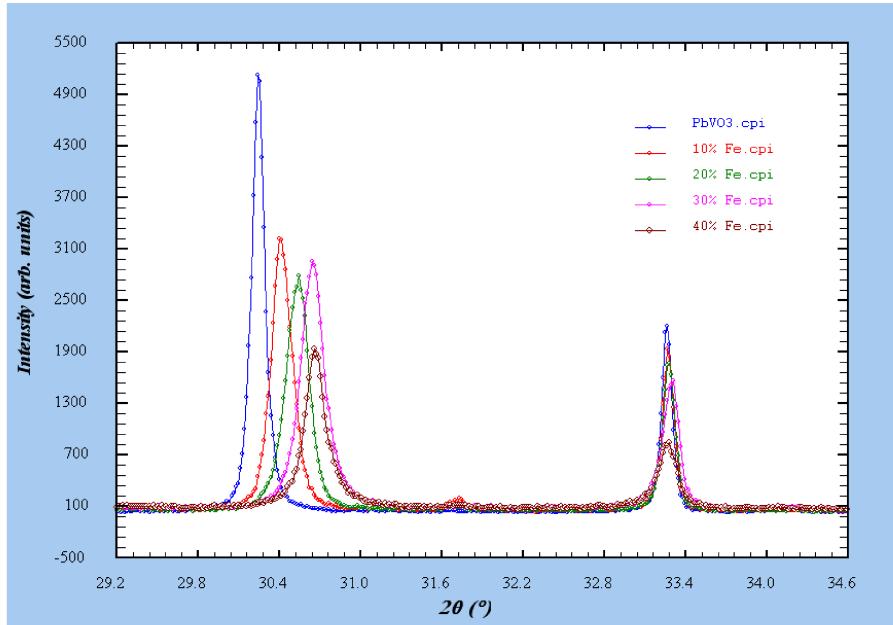
for the Ti series, a complete solid solution is obtained for $0 < x < 1$. Increasing the substitutions decreases c and increases a , thus converging towards the lattice parameters of $PbTiO_3$.

A linear variation of lattice parameters with the degree of substitution is observed

Shift in the position of diffraction peaks 101 (right) and 110 (left) for Ti series

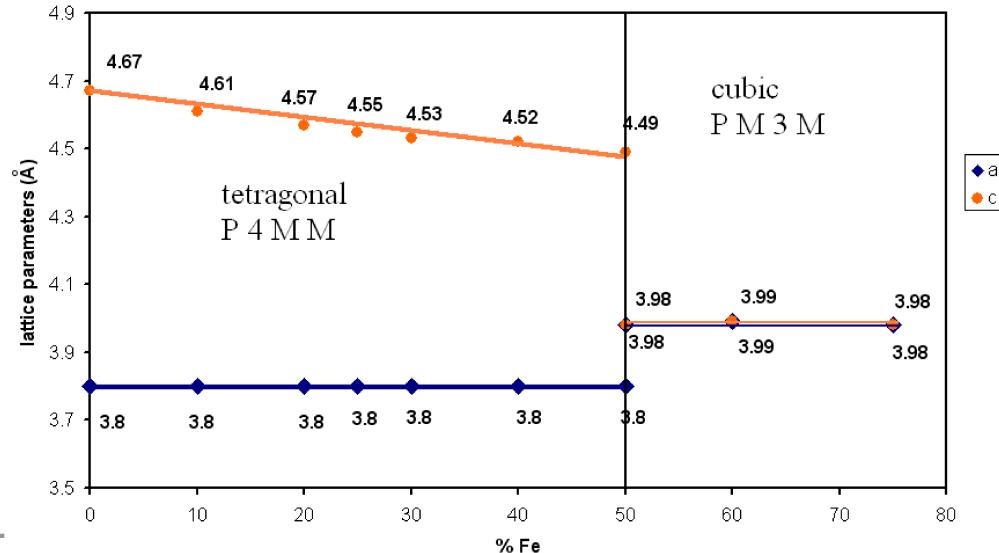


$Pb(V_{1-x} Fe_x) O_3$

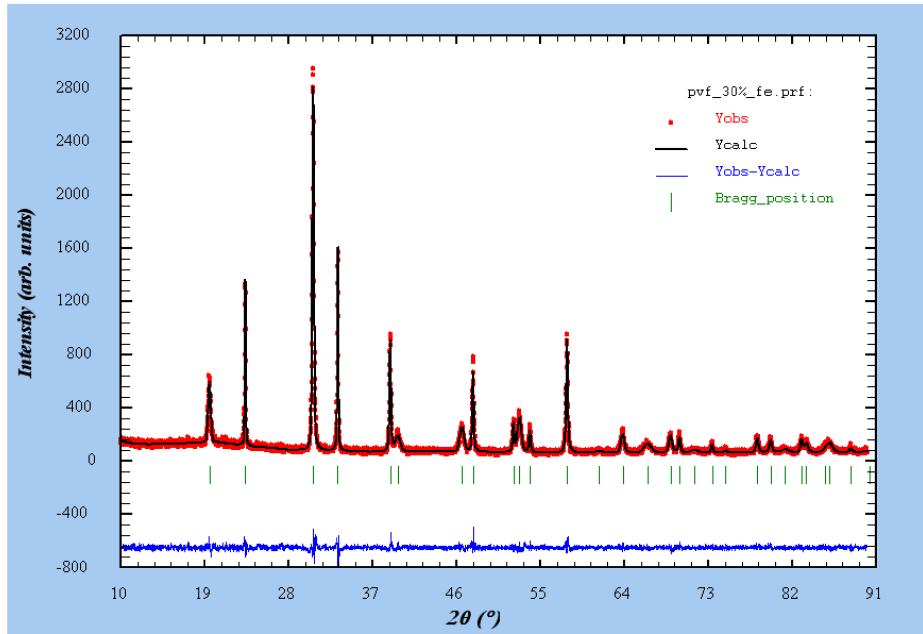


Shift in the position of diffraction peaks 101 (right) and 110 (left) for Fe series

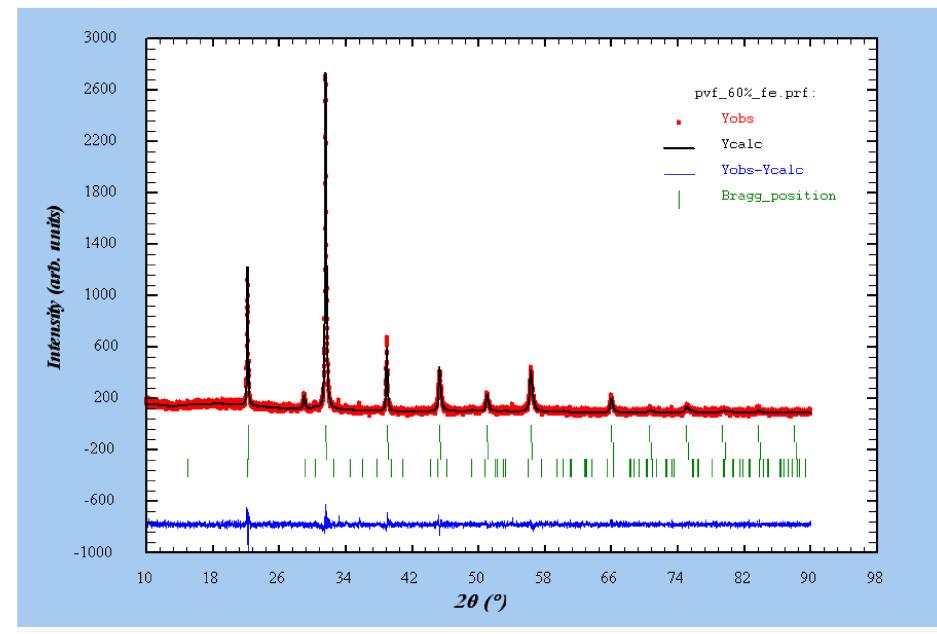
for the Fe series, the tetragonal structure is conserved until 50% substitution. Then, a new cubic phase is observed with unreacted products as impurities.



$Pb(V1-x Fe_x) O_3$

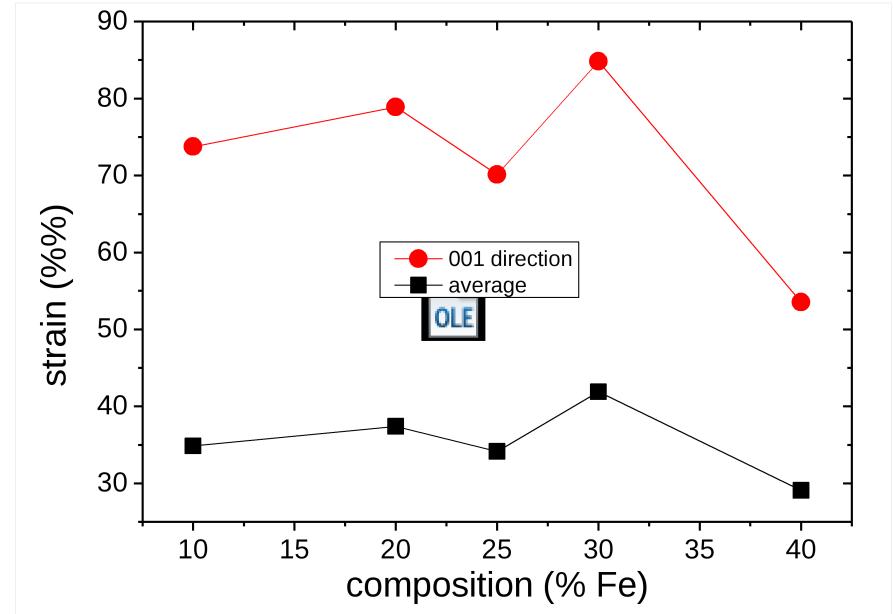
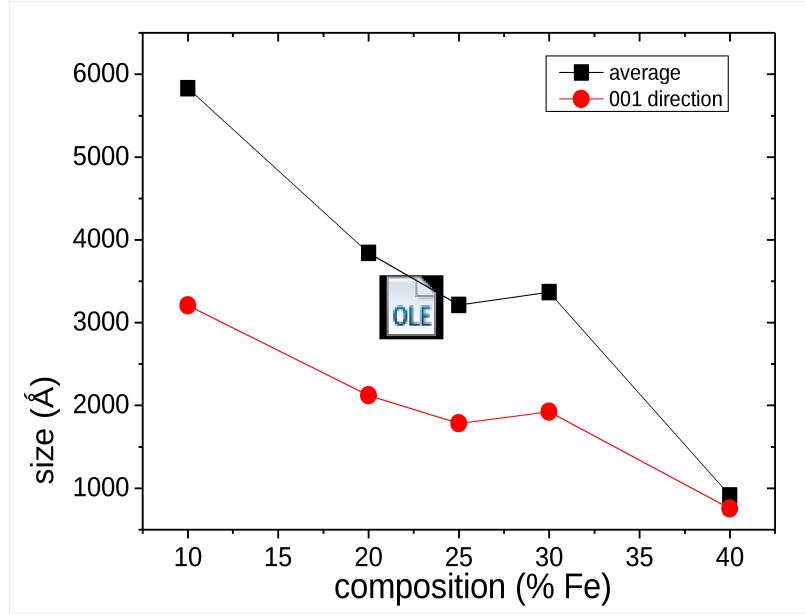


Rietveld refinement
on $PbV0.7Fe0.3O_3$ tetragonal
phase P4MM



Rietveld refinement
on $PbV0.4Fe0.6O_3$ cubic phase.
(SG: PM-3M, $a=3.98\text{\AA}$)

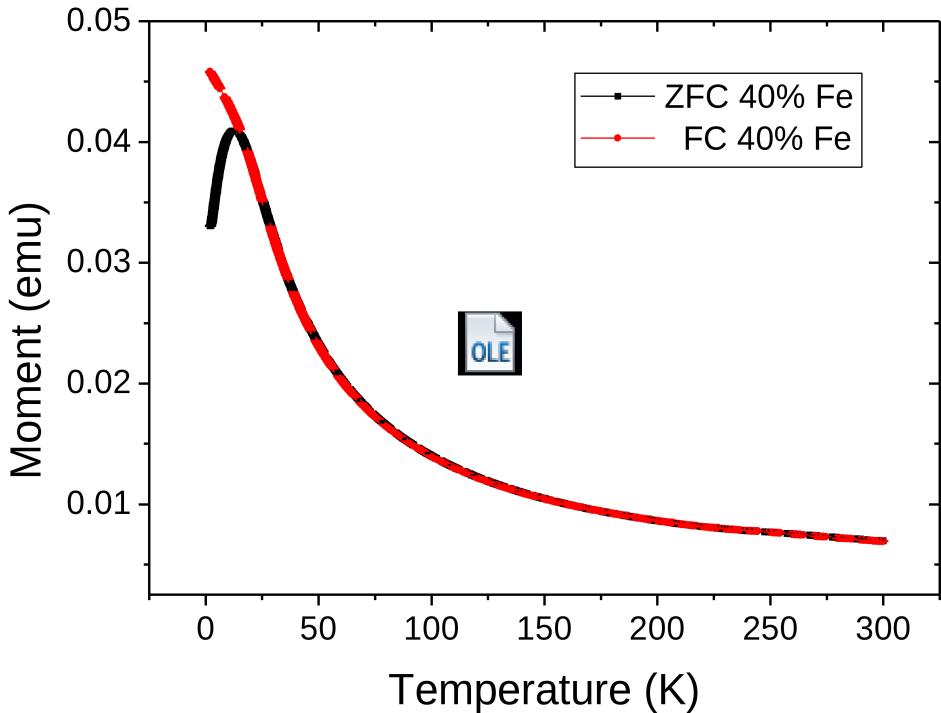
$Pb(V_{1-x} Fe_x) O_3$



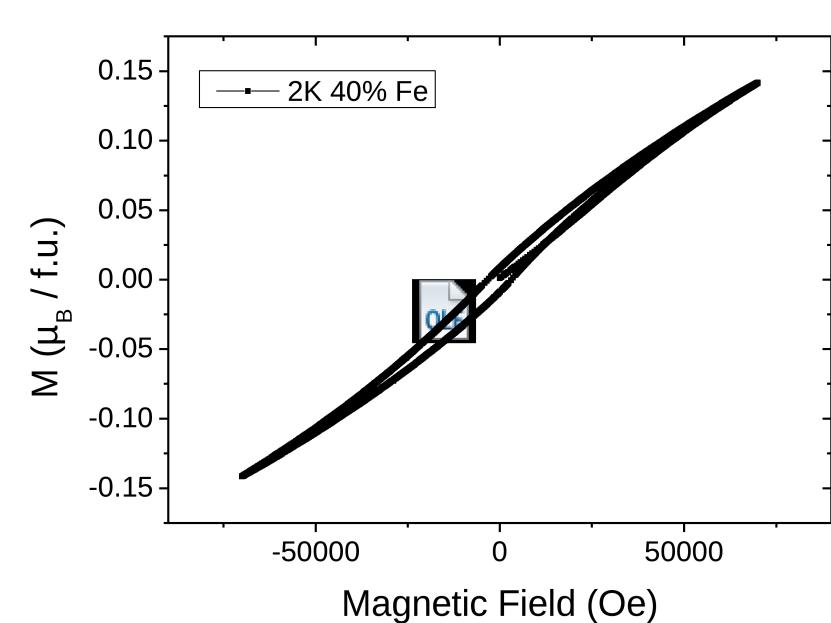
The grains are smaller and more mechanically strained along the c axis.

Anisotropic strain and particle size quantified by XRD are attributed to disorder due to V/Fe substitution.

Magnetic properties for $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$, $x=0-0.4$

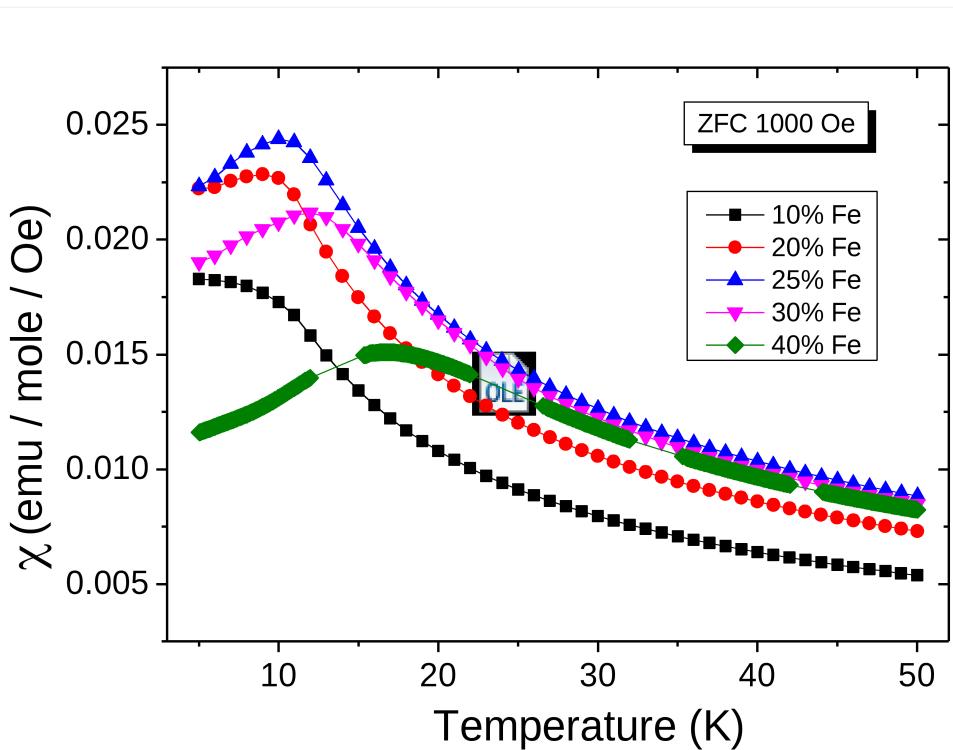


ZFC – FC curves show the presence of magnetic ordering transition

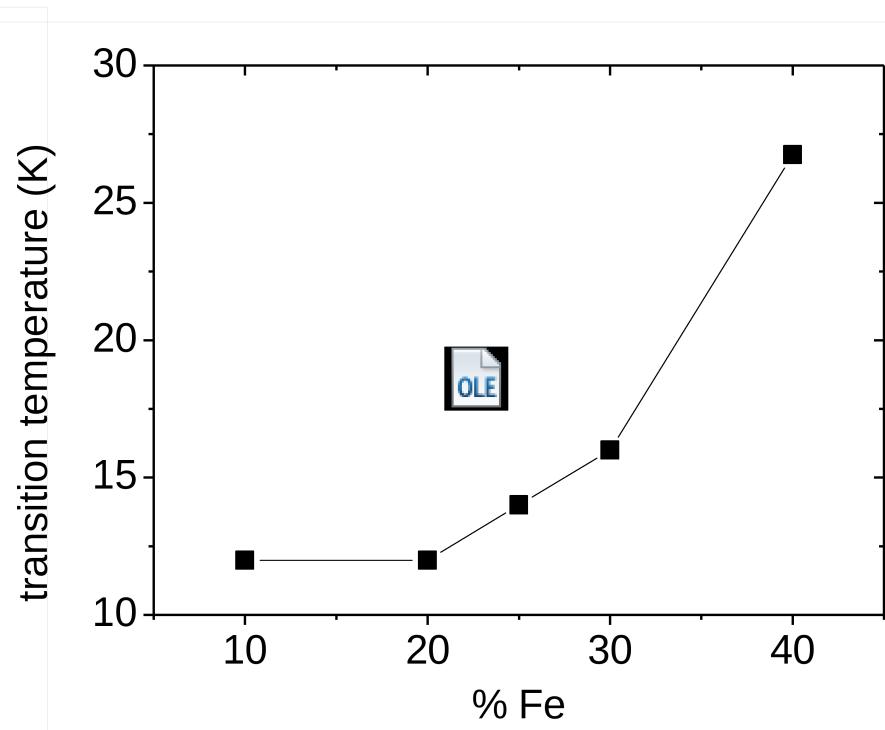


Magnetic hysteresis indicates the presence of a ferromagnetic component

Magnetic properties for $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$, $x=0-0.4$



The magnetic ordering transition is observed in all the iron doped samples



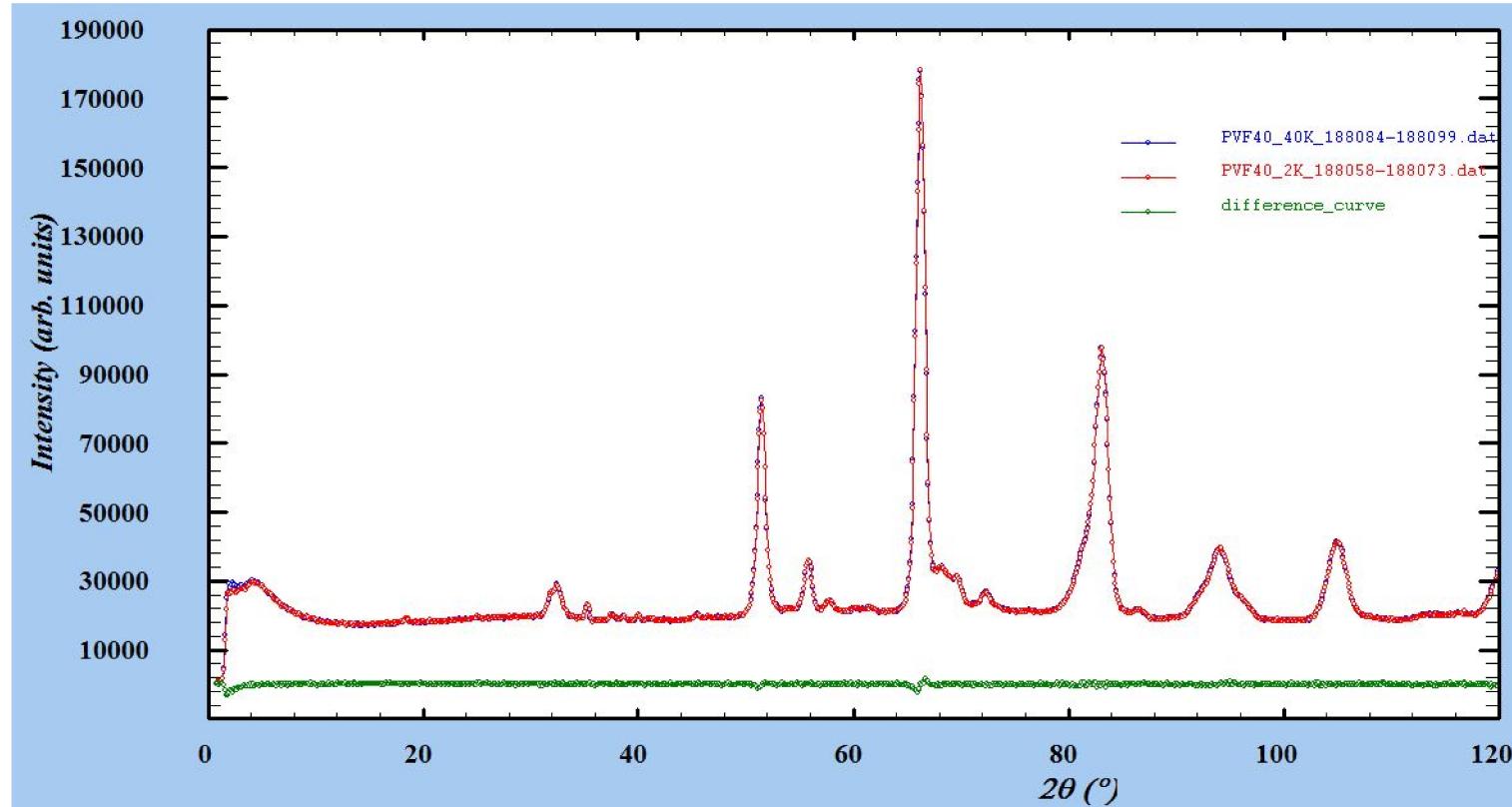
The transition temperature increases with $x(\text{Fe})$

Magnetic properties for $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$, $x=0\text{-}0.4$

Neutrons powder diffraction D1B ILL

No long range ordering

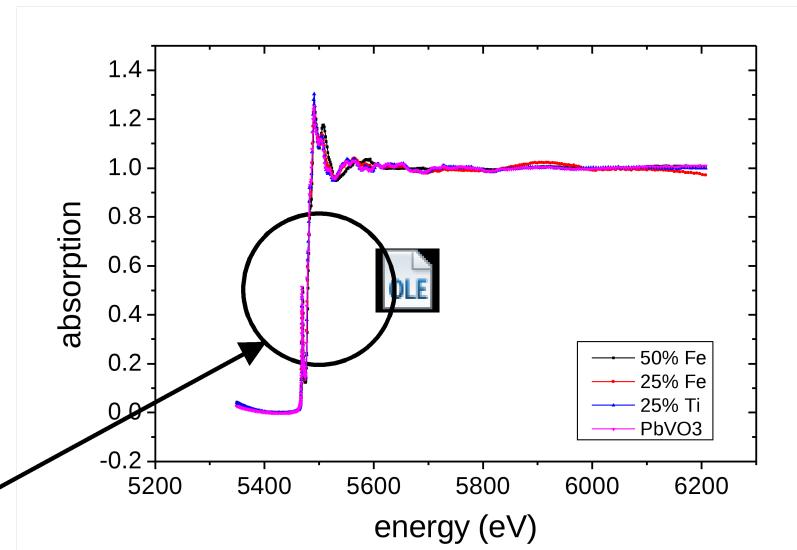
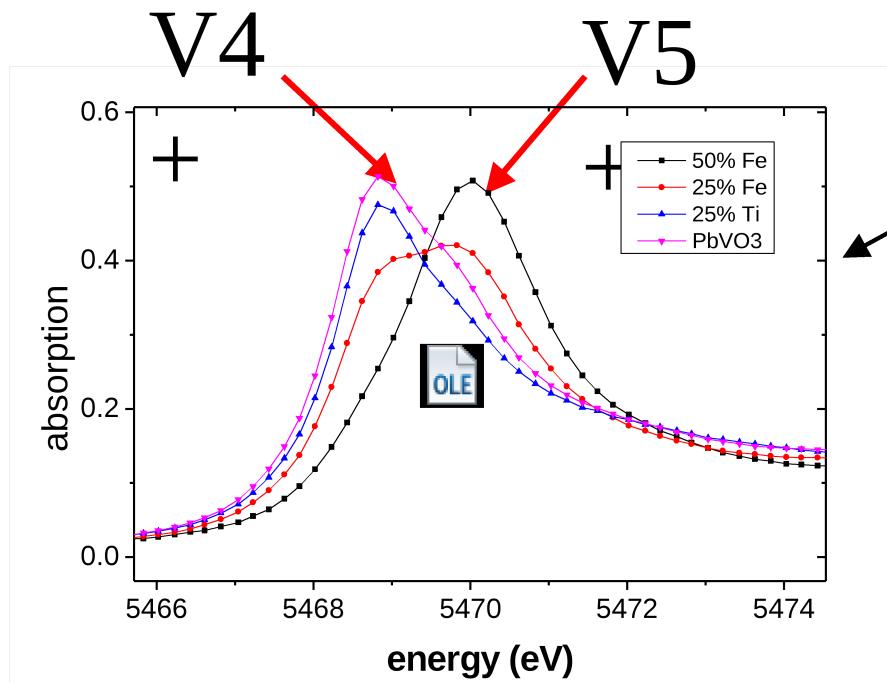
spin glass?



First result Mossbauer confirm magnetic Fe local ordering

X-Ray absorption spectroscopy

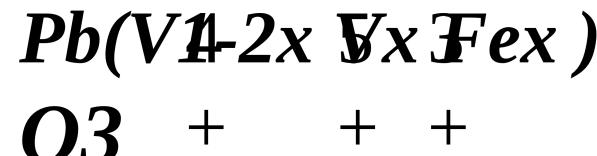
A change in the degree of oxidation for vanadium is observed as the concentration of iron is increased. No change is observed for Ti substitution.



BM32/FAME French CRG beamline of the ESRF, in transmission mode. (coll. J-L Hazemann, O. Proux)

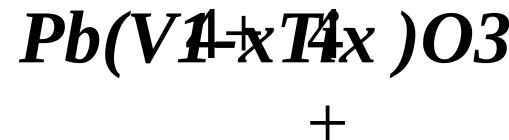
X-Ray absorption spectroscopy

It can be inferred that Fe³⁺ cations are substituted to V⁴⁺, leading to the general formula :

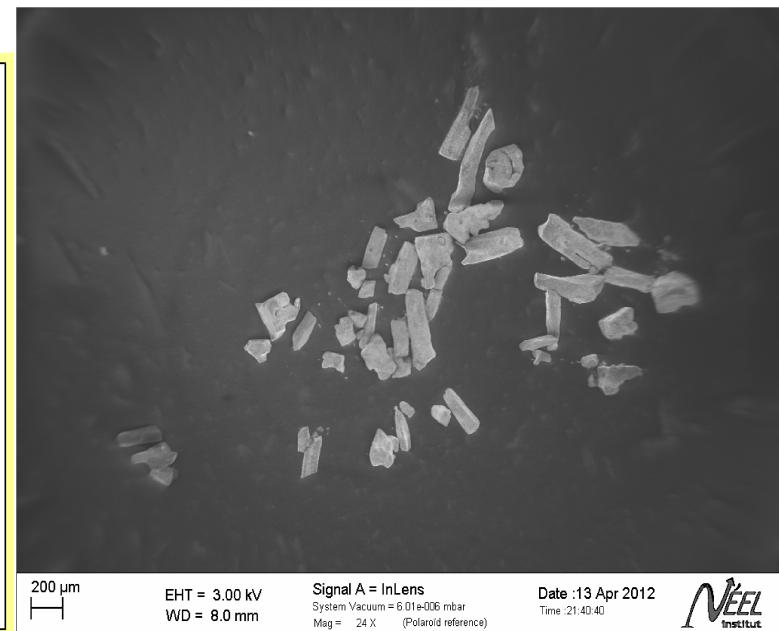
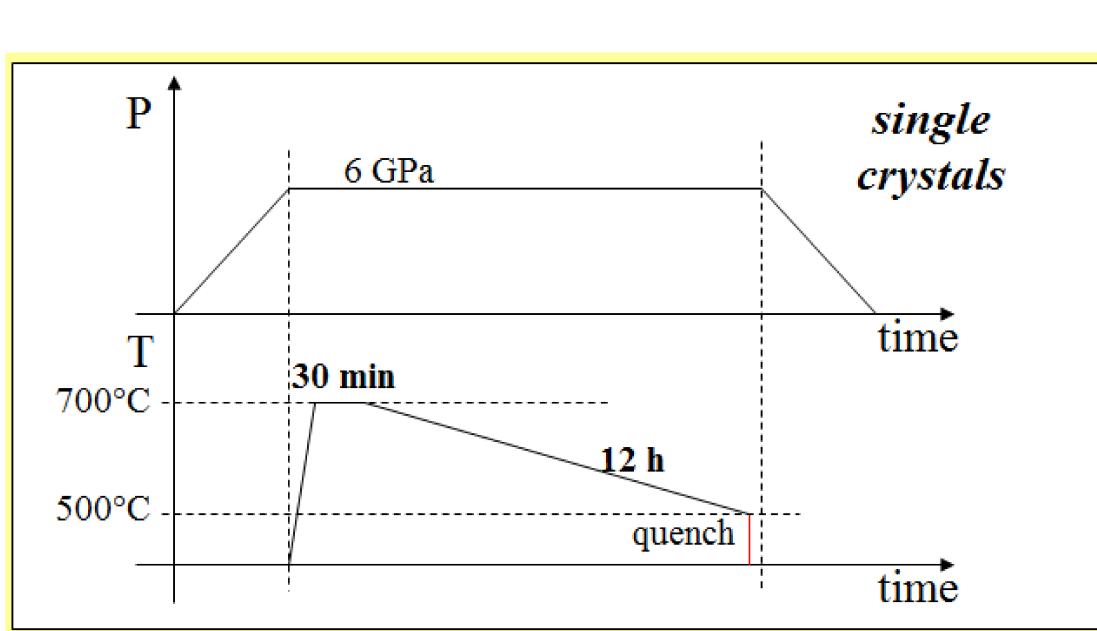


The solid solution has to stop at x=0.5.

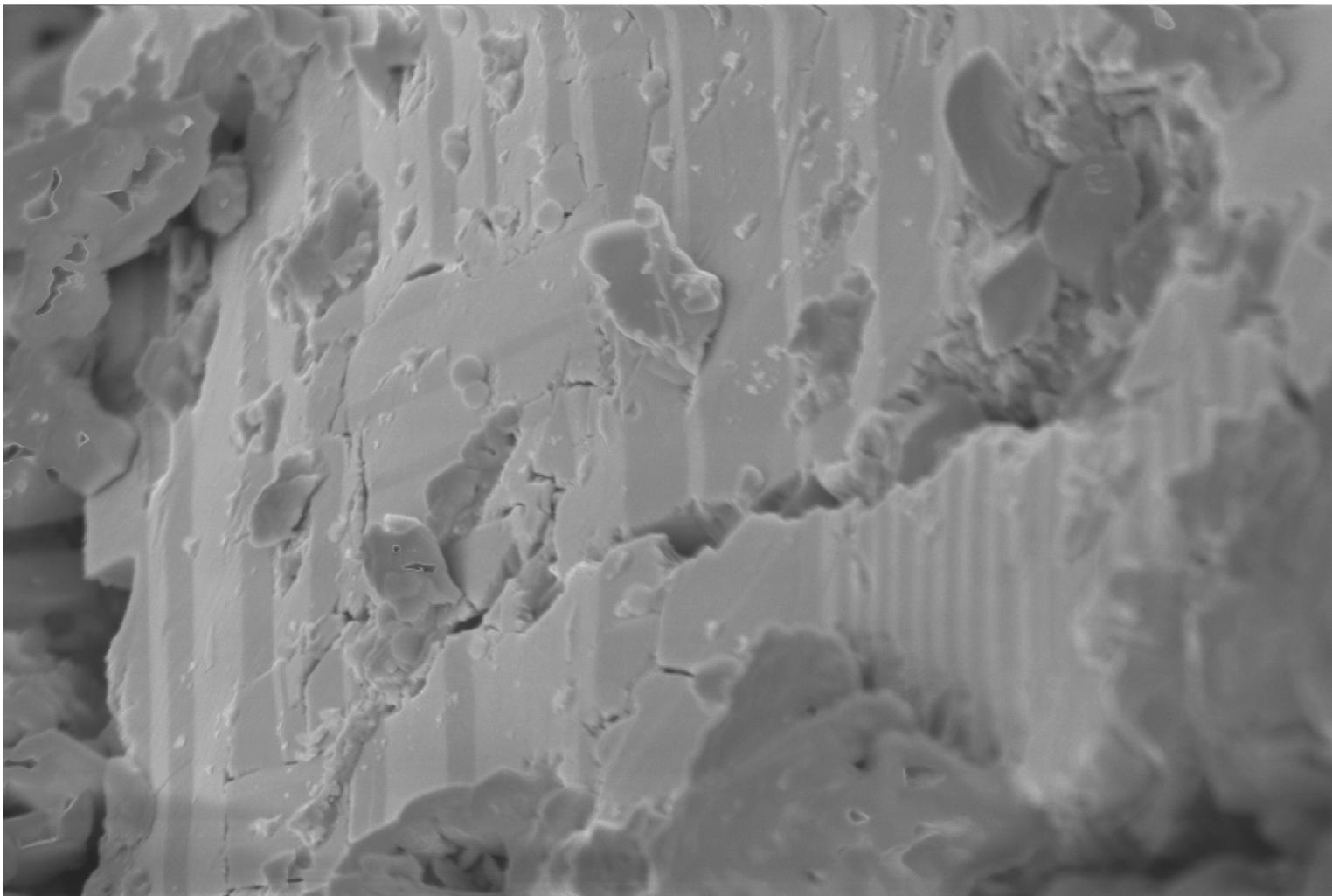
In the case of titanium, the substitution is isovalent, allowing a complete solid solution:



Single crystals were obtained by hydrothermal method in CONAC 10% wt water added to the mixture and slow cooling under pressure.



HP-HT Single crystal synthesis



200 nm



EHT = 3.00 kV
WD = 7.4 mm

Signal A = InLens
System Vacuum = 4.98e-006 mbar
Mag = 20.67 KX (Polaroid reference)

Date : 13 Apr 2012
Time : 22:07:44

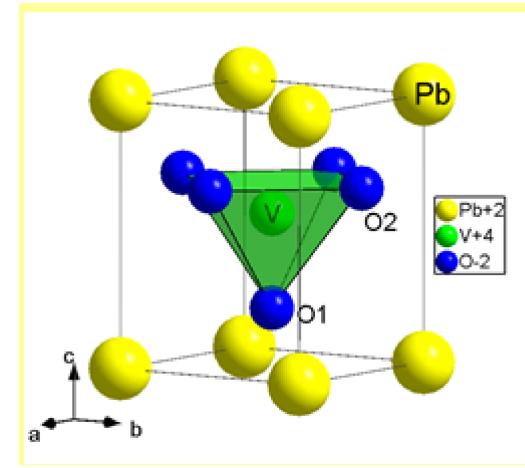
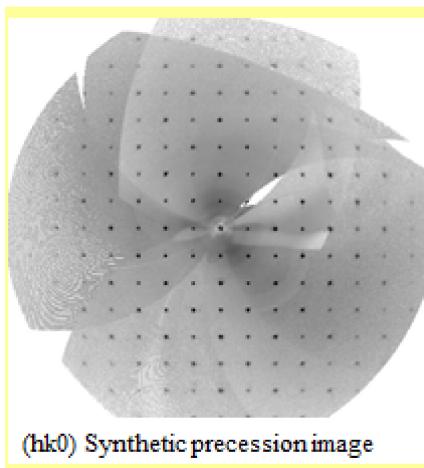
HP-HT Single crystal synthesis

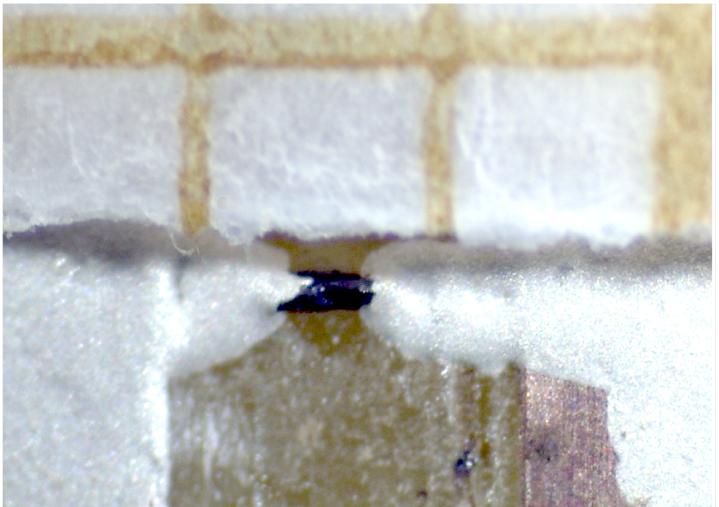
Single crystal XRD Structure resolution

Bruker Kappa ApexII, AgK α , $\theta_{\text{max}} = 34.85^\circ$, wR=2.8%, gof=1.6, 405 refl, 14param.
Racemic twin, 80/20%

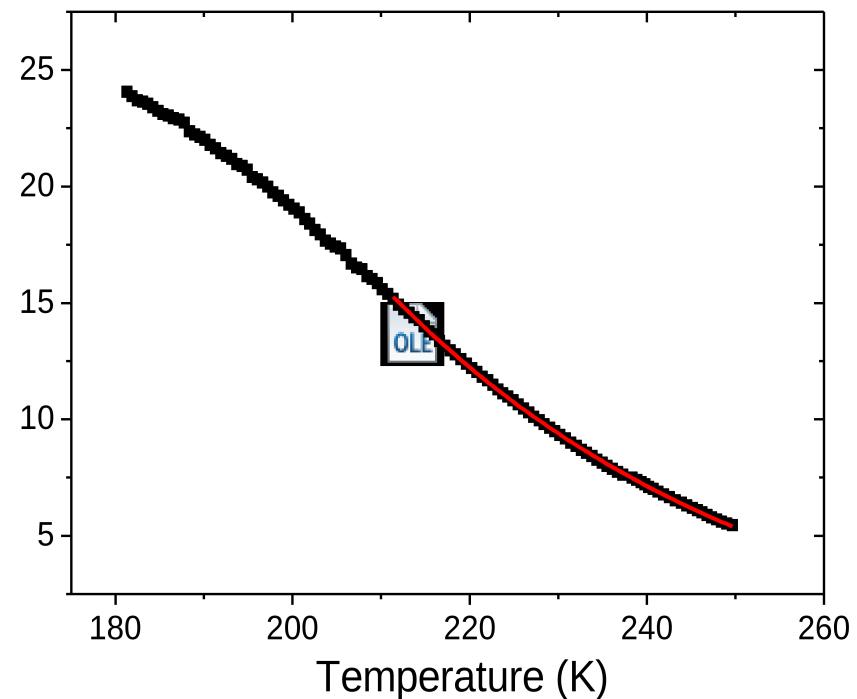
Atom positions					Anisotropic displacement parameters (\AA^2)		
	Wyckoff	x	y	z	U_{11}	U_{22}	U_{33}
Pb	1a	0	0	0	0.00759(8)	0.00759(8)	0.01299(10)
V	1b	0.5	0.5	0.5690(3)	0.0061(3)	0.0061(3)	0.0126(5)
O1	1b	0.5	0.5	0.2153(19)	0.013(2)	0.013(2)	0.015(3)
O2	2c	0.5	0	0.6900(14)	0.0088(19)	0.0086(19)	0.017(2)

Distances (\AA)	
Pb-O1(x4)	2.867(3)
Pb-O2(x4)	2.386(4)
V-O1	1.649(9)
V-O1	3.013(9)
V-O2(x4)	1.9810(19)



Resitivity measurements

The measurement of resistivity vs. T shows a semi-conducting behaviour (decrease of resistivity with temperature) with a possible activation energy of 0.2 eV.



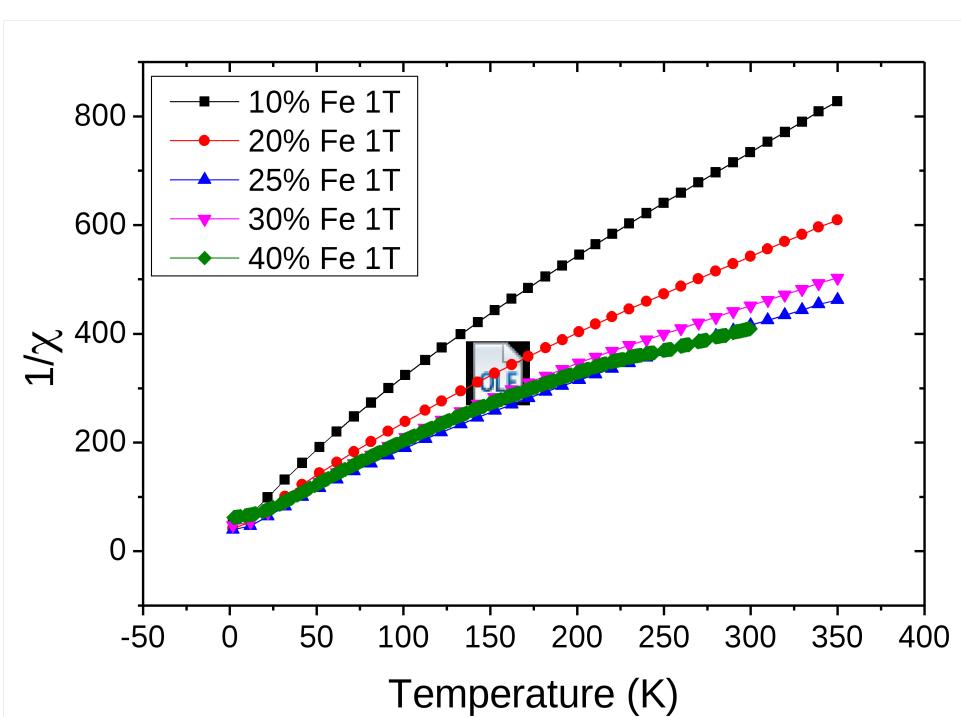
Conclusions

- the substitution of V by Fe and by Ti was studied. In the case of Fe a new cubic phase was discovered for $x \geq 0.5$.
- anisotropic strain and particle size quantified by XRD, attributed to disorder due to V/Fe substitution.
- preliminary XAS data indicate heterovalent V/Fe and isovalent V/Ti substitution
- single crystals of PbVO₃ were grown at high pressure. Their structure was refined by XRD.

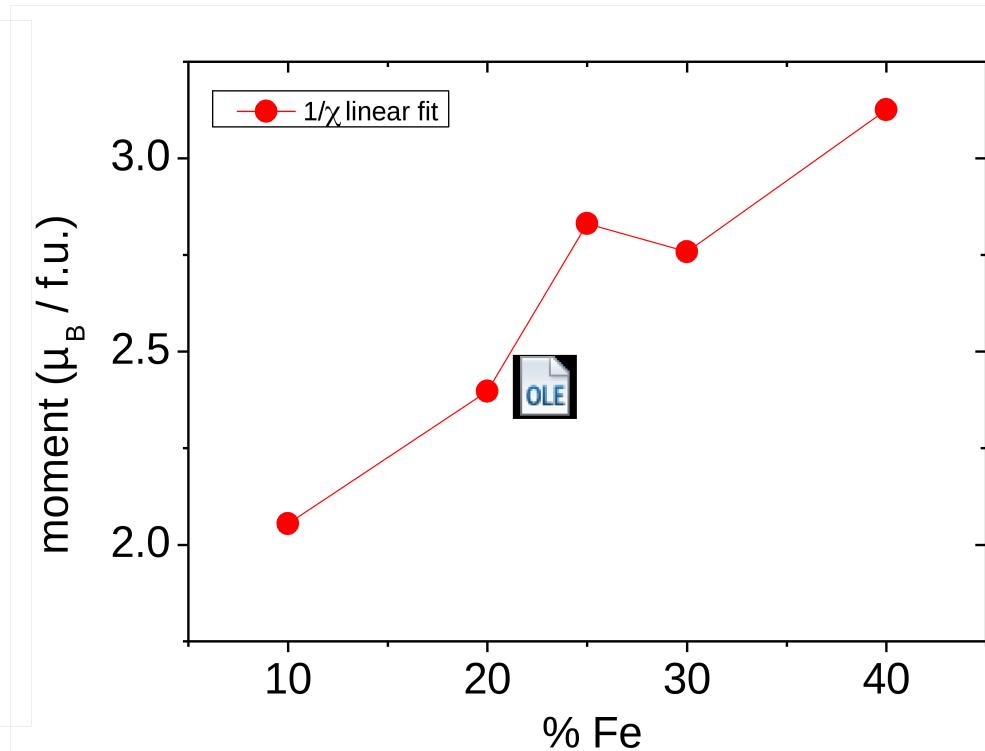
- specific heat measurements
- electric polarization
- neutron powder diffraction
- Mössbauer spectroscopy

- Rendez vous demain pour d'autres histoires de multiferroiques.....

Magnetic properties for $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$, $x=0-0.4$



$1/\chi$ vs. T plot shows antiferromagnetic interactions, magnetization increases with $x(\text{Fe})$



Magnetic moment per f.u. (μ_B) from Curie-Weiss fit indicate a too large moment for Fe^{3+}