

Crystal Chemistry, Properties and Applications of Phosphates

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Crystallography for the next generation

The Legacy of the International Year of Crystallography

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Outline

- General introduction on phosphates
- Structures and properties of some phosphates
 - * Oxyphosphates
 - * Monophosphates
 - * Diphosphates

General introduction on phosphates

- Use of phosphates
- Classification of phosphates

Uses of phosphates

Inorganic phosphates exist in both crystalline and glassy form.

P_2O_5 is a forming oxide like SiO_2 and B_2O_3 .

Phosphate-based materials have potential applications in many fields :

Biomaterials

Electrodes for batteries

Optical components : Lasers, LEDs,

Catalysts

Stock of radioelements

Pigments

Cosmetics,.....

Some important phosphate families:

Apatite : Biomaterials

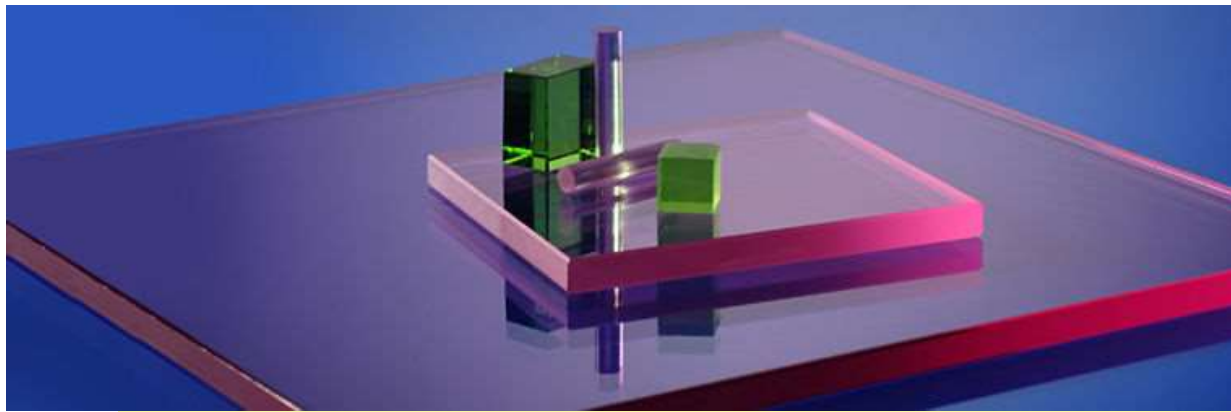
Nasicon (Na super ionic conductor) : ionic conductors, electrode materials, photocatalysts, sensors

Zeolite : Catalysis,...

Olivine : Li-batteries

KTP (KTiOPO_4) : Non Linear Optical Materials

Glasses : Lasers, bioglasses , stock of nuclear waste



Lasers



Electric vehicles



Luminophores



Pigments



Biomaterials

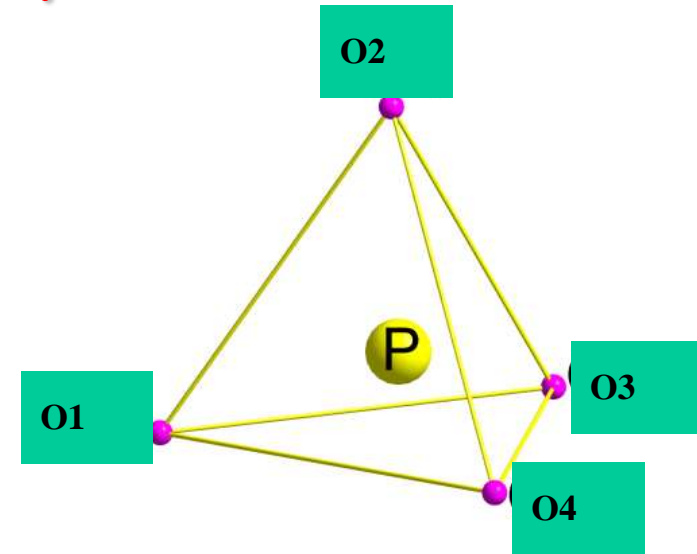
Classification of phosphates*

The basic unit of phosphate structures is the PO_4 tetrahedron.

$\text{O/P} > 4$: **Oxyphosphates** :
 $\text{K}(\text{TiO})(\text{PO}_4)$; $\text{Ca}_{10}\text{O}(\text{PO}_4)_6$

$\text{O/P} = 4$: **Monophosphates** :
 Na_3PO_4 ; FePO_4

$\text{O/P} < 4$: **Condensed Phosphates*** :
 $\text{Na}_4\text{P}_2\text{O}_7$; $\text{Na}_5\text{P}_3\text{O}_{10}$; NaPO_3

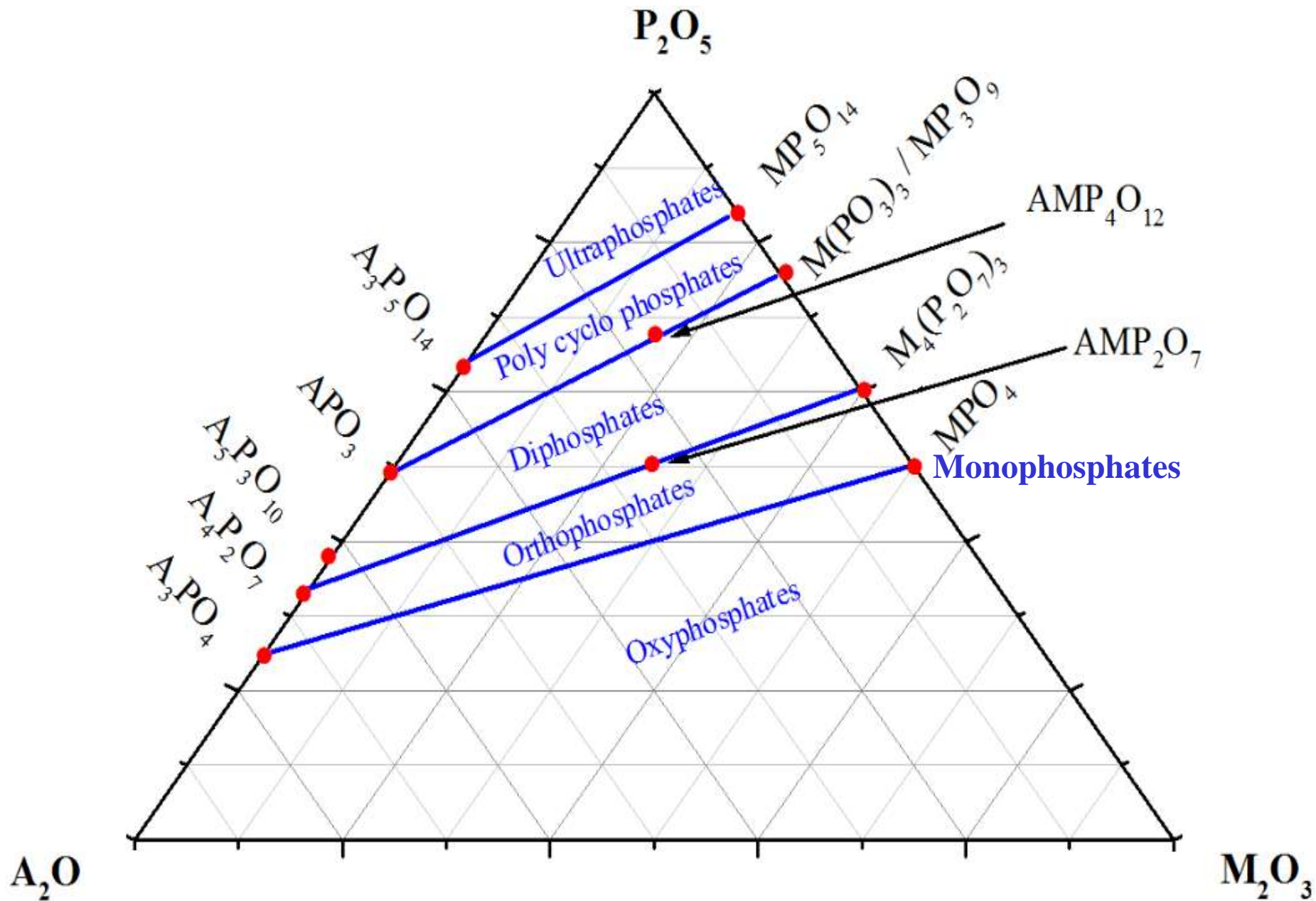


Remarks:

$\text{W}^{\text{VI}}\text{P}_2\text{O}_8$ ($\text{O/P}=4$) : $\text{W}^{\text{VI}}\text{O}(\text{P}_2\text{O}_7)$ oxydiphosphate

Mixt anions : $\text{Li}_9\text{Fe}_3(\text{P}_2\text{O}_7)_3(\text{PO}_4)_2$

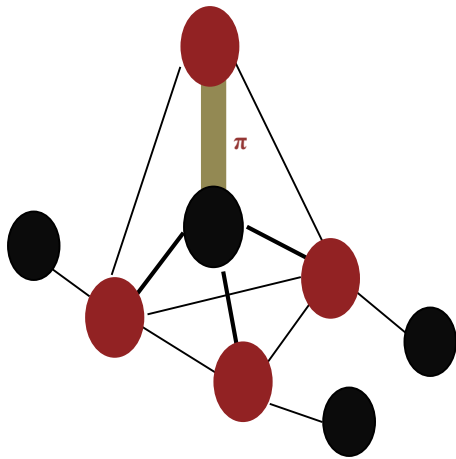
* A. Durif. Crystal Chemistry of Condensed Phosphates, (1995), NY-L, Plenum Press.



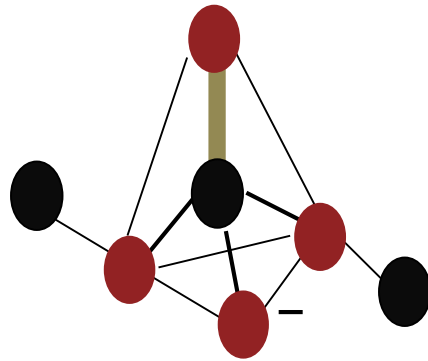
4 kinds of PO_4 groups

Q^n notation

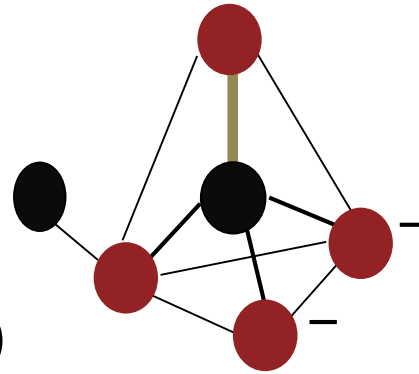
n is the number of the bridging oxygens



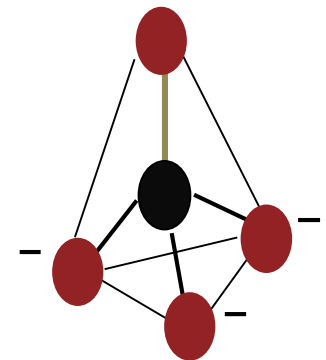
Branching group
 Q^3 (P_2O_5)



Middle group
 Q^2 (NaPO_3)



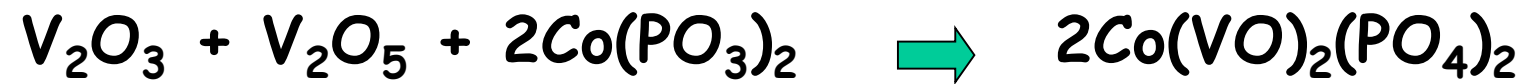
Terminal group
 Q^1 (TiP_2O_7)



Isolated group
 Q^0 (FePO_4)

Oxyphosphates



Powder :

- Alpha phase (α) : $T = 700^\circ \text{ C}$ (under vacuum)
- Beta phase (β) : $T = 900^\circ \text{ C}$ (under vacuum)

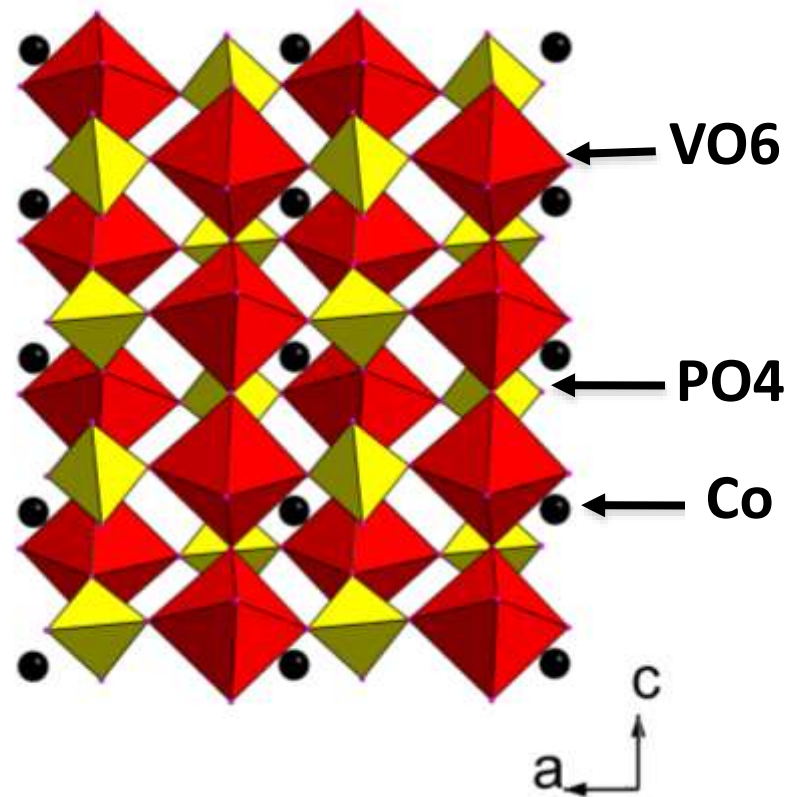
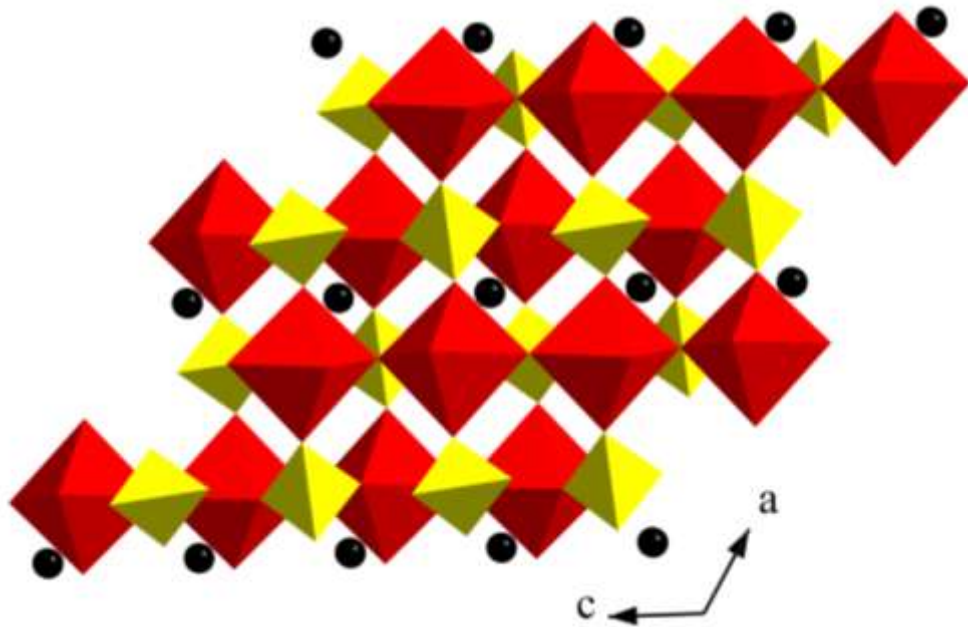
Single crystals :

- Alpha phase (α) : Crystalline powder of α -phase contains microcrystals (dimensions : $\sim 20 \mu\text{m}$)
- Beta phase (β) : Melting of β powder at 1100° C (under vacuum) + slow cooling (5° C/h) \Rightarrow single crystals
(dimensions: $\sim 80/60/60 \mu\text{m}$)

Syntheses and Crystal Structures of new vanadium (IV) oxyphosphates $\text{M}(\text{VO})_2(\text{PO}_4)_2$ with $\text{M} = \text{Co}, \text{Ni}$.

S. Kaoua, P. Gravereau, J. P. Chaminade, S. Pechev, S. Krimi, and A. El Jazouli. J. State Sciences, 11 (3), 2009, 628 - 634.

Structure of $\text{Co}(\text{VO})_2(\text{PO}_4)_2$

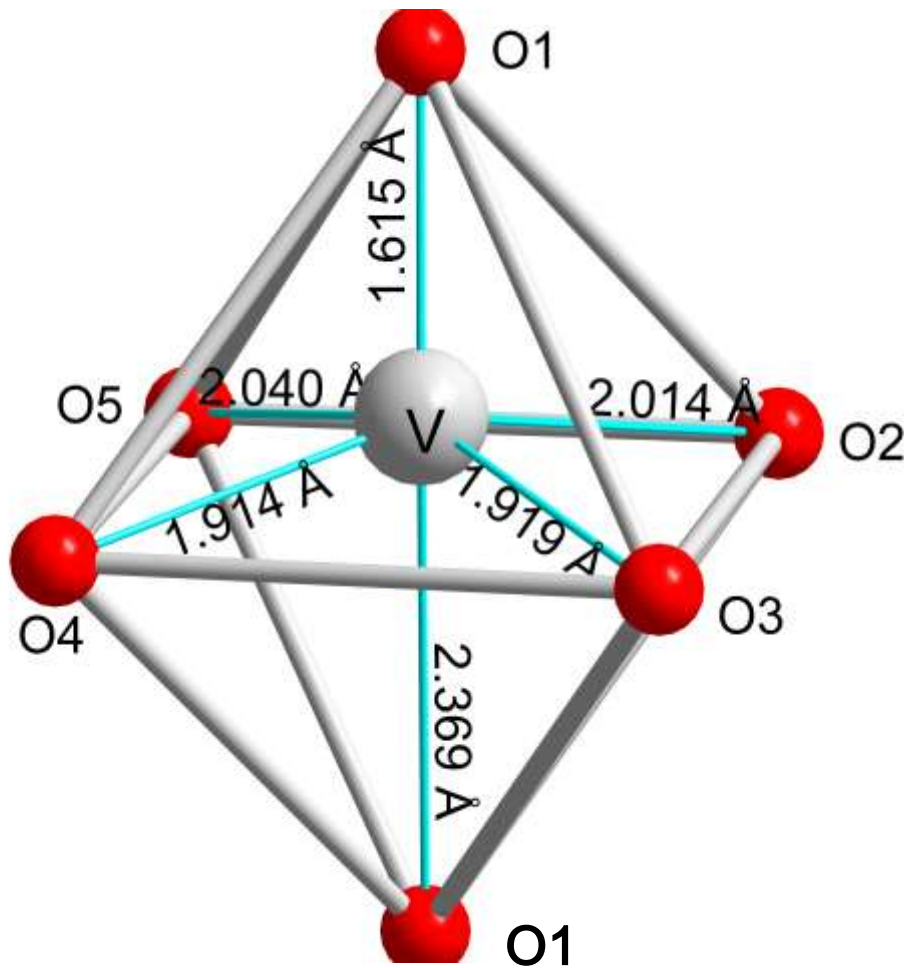


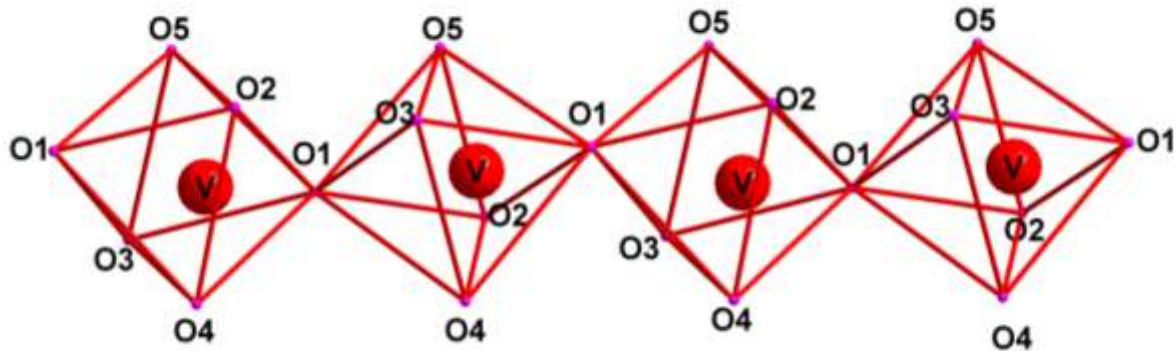
$\text{Co}(\text{VO})_2(\text{PO}_4)_2$

Vanadium atom is displaced from the centre of the octahedron giving rise to an alternating long (2.369\AA) and short (1.616\AA) V-O1 bonds. The four remaining V-O bond distances have intermediate values ranging between 1.914\AA and 2.040\AA .

$$R(\text{O}^{2-}) + R_i(\text{V}^{4+}) = 1.96\text{\AA}$$

VO_6





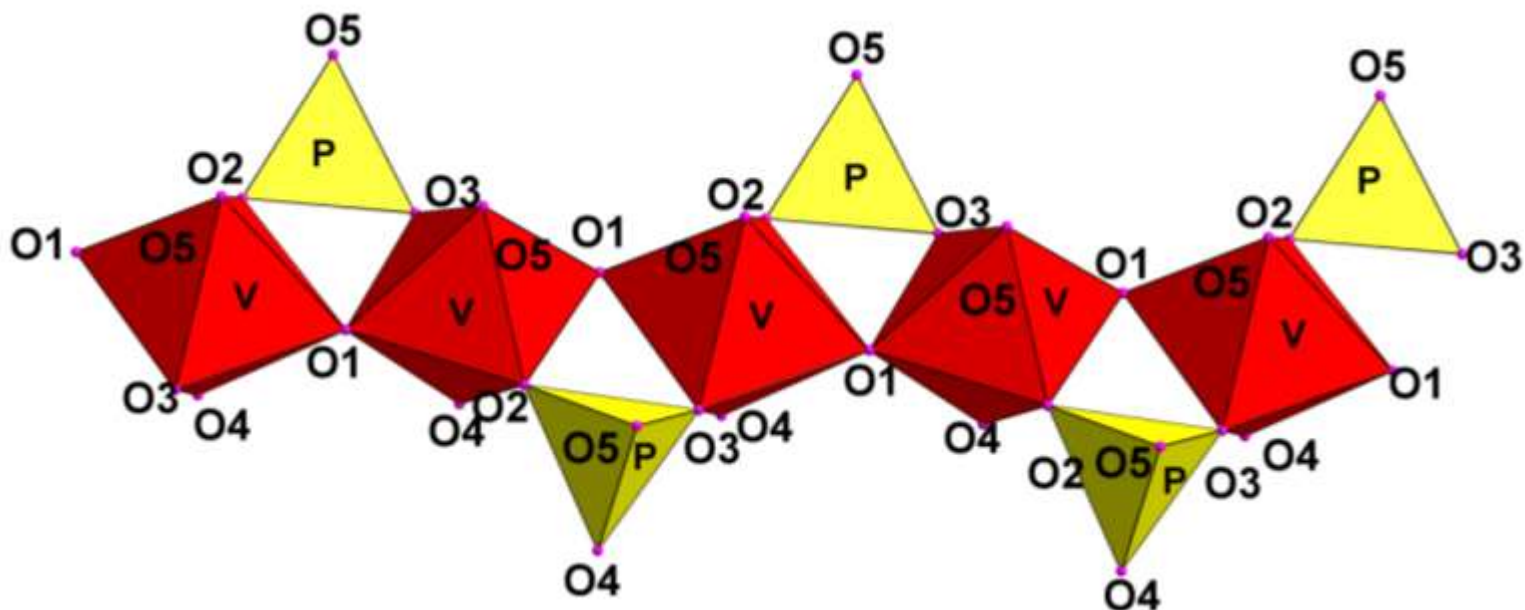
(VO_6) octahedra linked by corners along c axis



Vanadyl ion $(VO)^{2+}$



Vanadyl phosphate

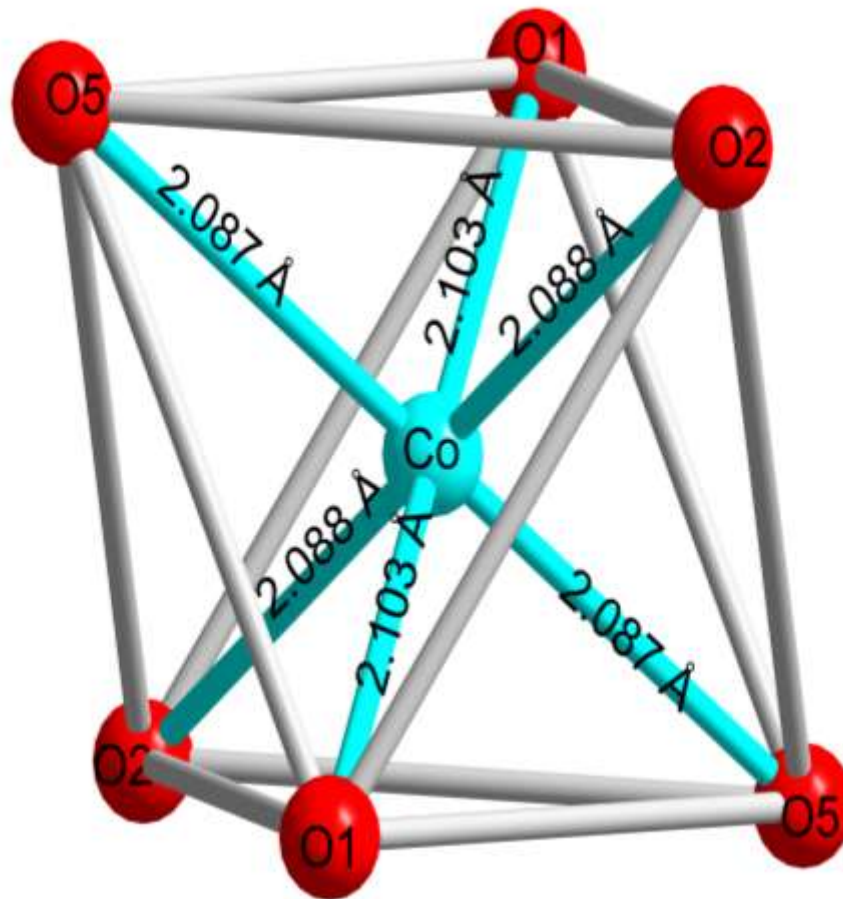


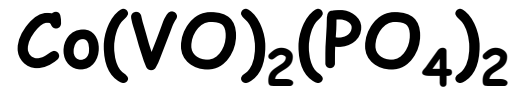
(VO_6) octahedra and PO_4 tetrahedra in $\alpha\text{-M}(\text{VO})_2(\text{PO}_4)_2$ ($M = \text{Co}, \text{Ni}$)

$\text{Co}(\text{VO})_2(\text{PO}_4)_2$

- Co^{2+} ion: triangular based antiprism, located between two VO_6 octahedra
- Co-O distances : 2.087 Å - 2.103 Å
- Ionic radii sum of O^{2-} and Co^{2+} : 2.12 Å
- Slight covalent character of Co-O bonds

CoO_6



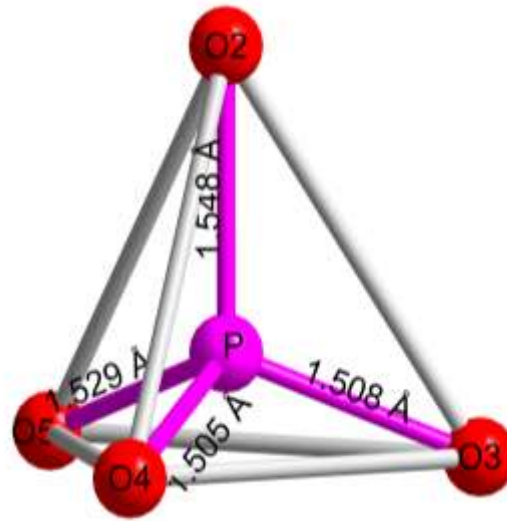


PO_4 tetrahedra are quite regular

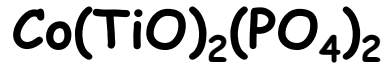
P-O distances : 1.506 Å - 1.548 Å

O-P-O angles : 106.5° - 112.2° .

PO_4



Raman spectra



Ti-O : 1.70 – 2.30 Å

-Ti-O-Ti-O-Ti-O-Ti-

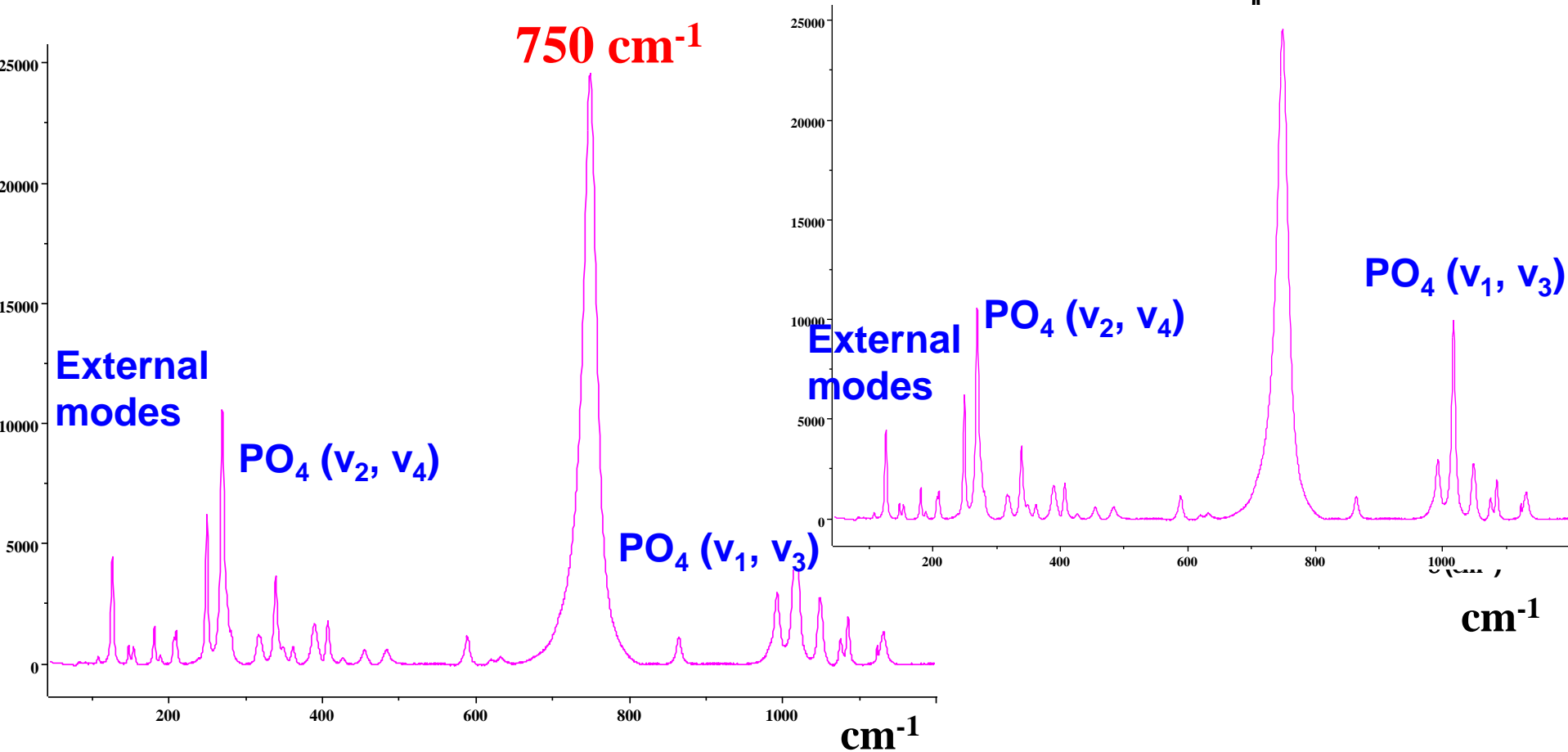
750 cm^{-1}



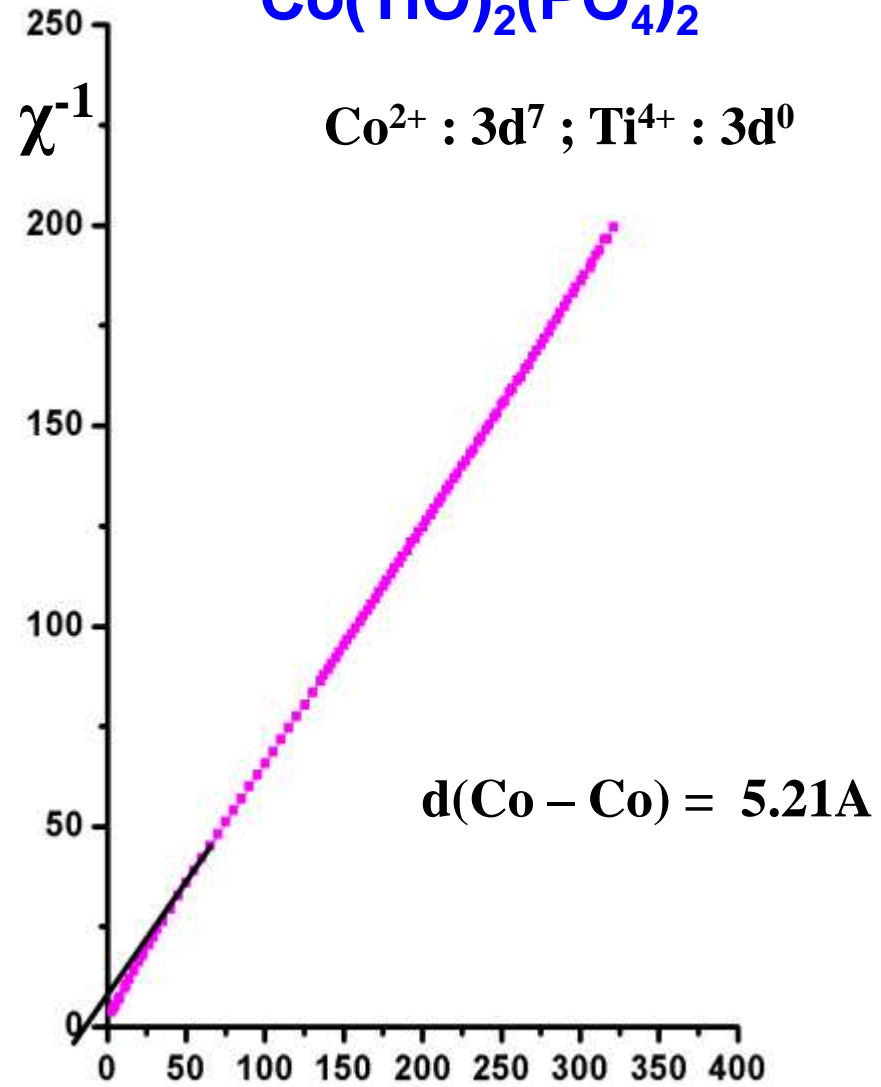
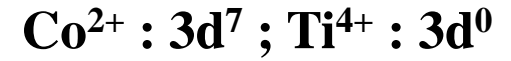
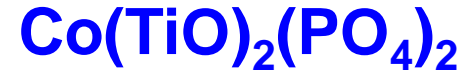
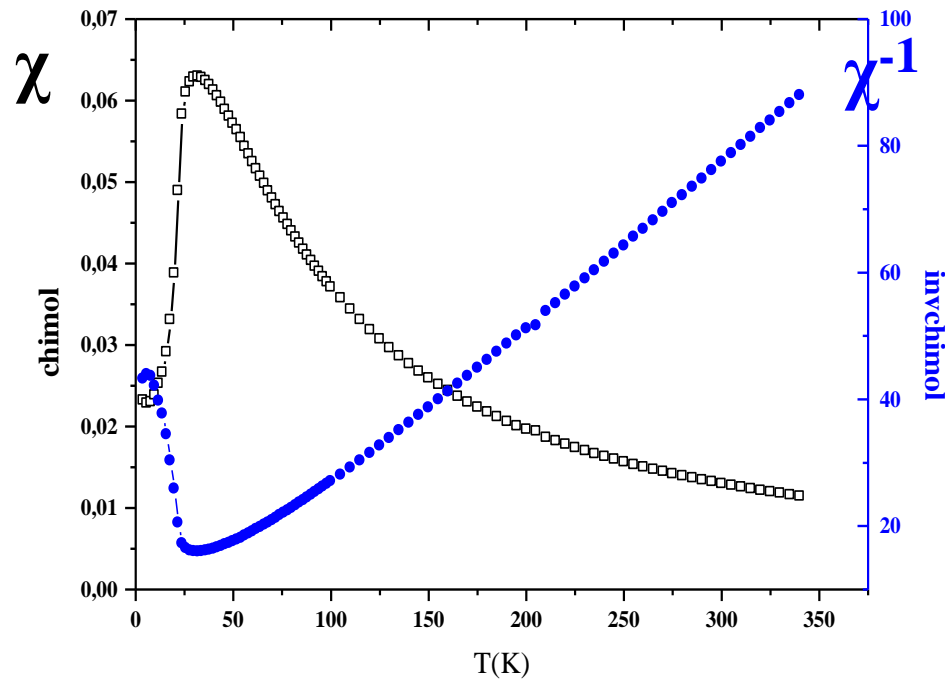
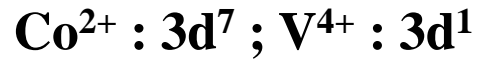
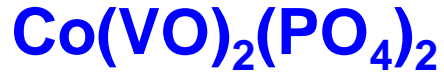
V-O : 1.62 – 2.25 Å

-V-O-V-O-V-O-V-

850 cm^{-1}



Magnetic properties



$d(\text{Co} - \text{Co}) = 5.21 \text{ \AA}$



Synthesis, structure and magnetic properties

Powder:

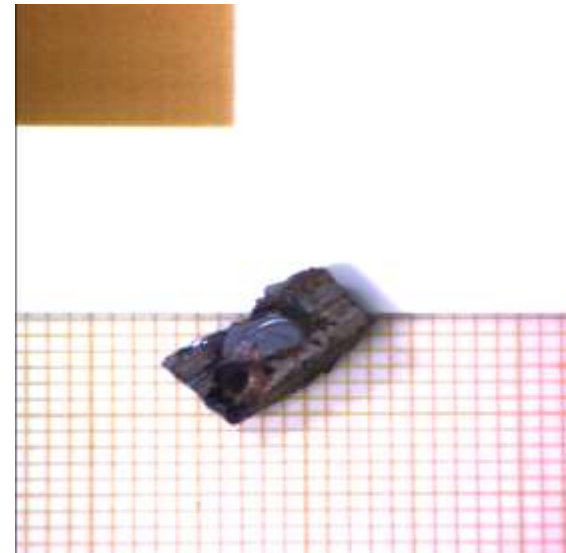
Co-precipitation : $\text{Pb}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$

Solid state : SrCO_3 (CaCO_3), Fe_2O_3 and $(\text{NH}_4)\text{HPO}_4$

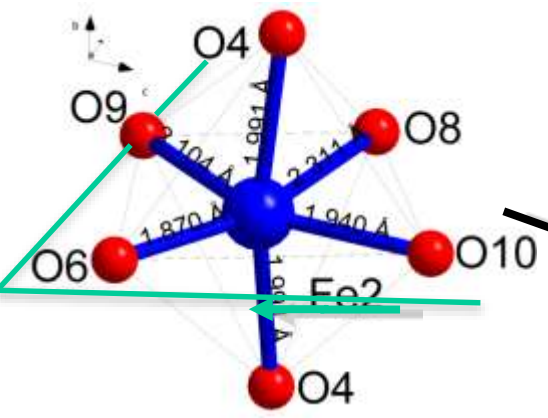
Thermal treatments 100°C , 200°C , 400°C and 880°C , 72 h
Powder color : red

Single crystal:

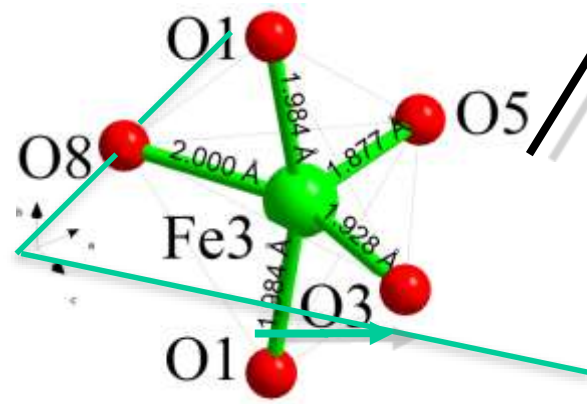
Combination of flux and Bridgman methods



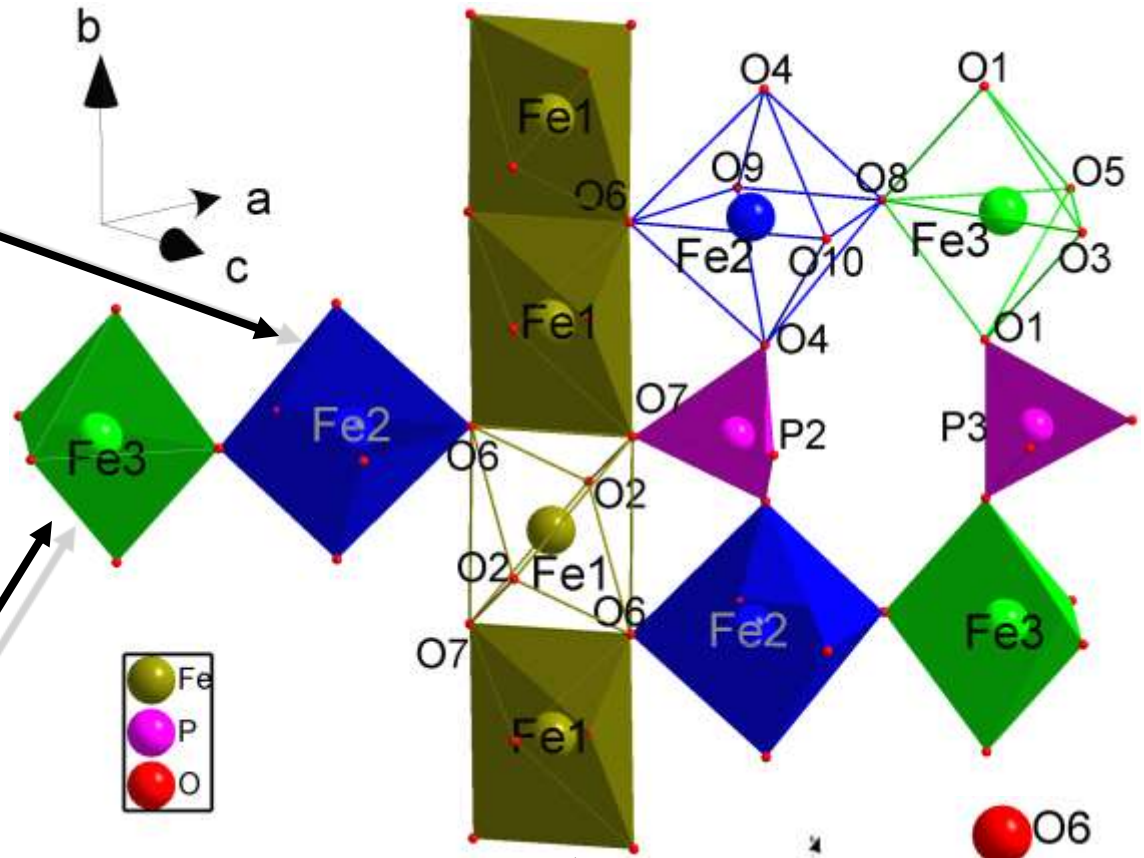
PbFe₃O(PO₄)₃ structure determination by single crystal XRD (1)



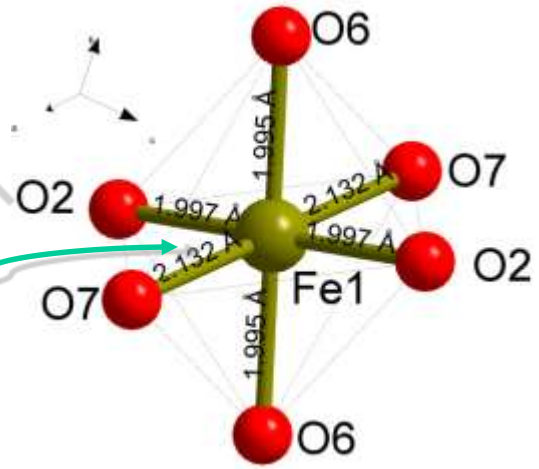
Mirror plane *m* passing through O6, O8, O9 and O10 (1.9% deviation from perfect octahedron/1.8% deviation from inversion point)



Mirror plane *m* passing through O3, O5 and O8 (4.2% deviation from perfect square base pyramid/6% deviation from perfect triangle bi-pyramid/21.4% deviation from inversion point)

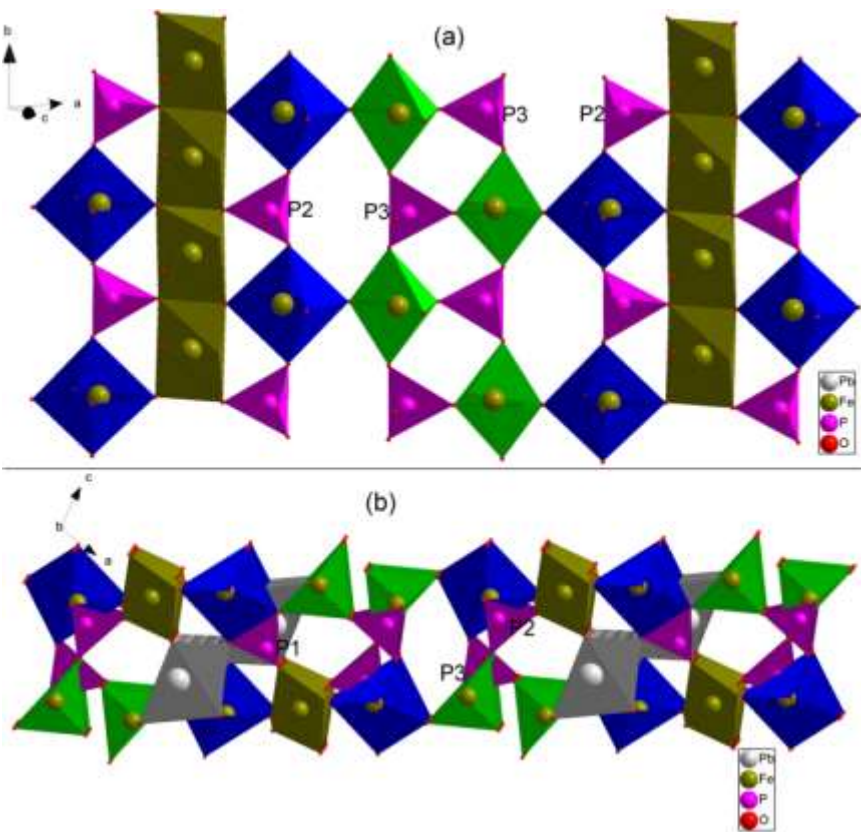


Infinite chain parallel to *b*

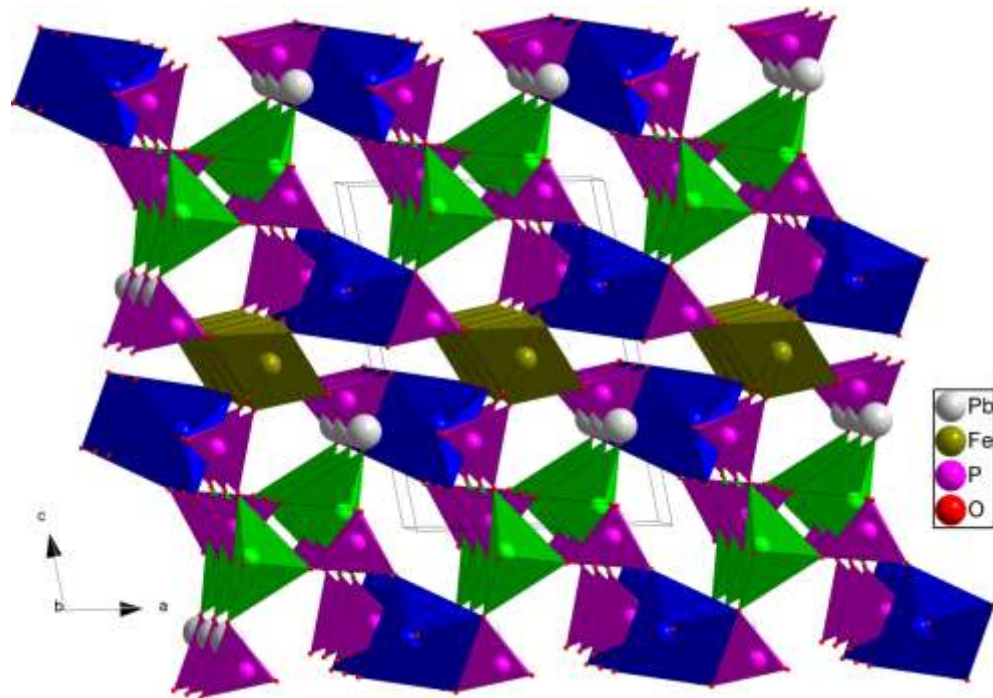


Inversion point (1% deviation from perfect octahedron)

Structure of $\text{PbFe}_3\text{O}(\text{PO}_4)_3$

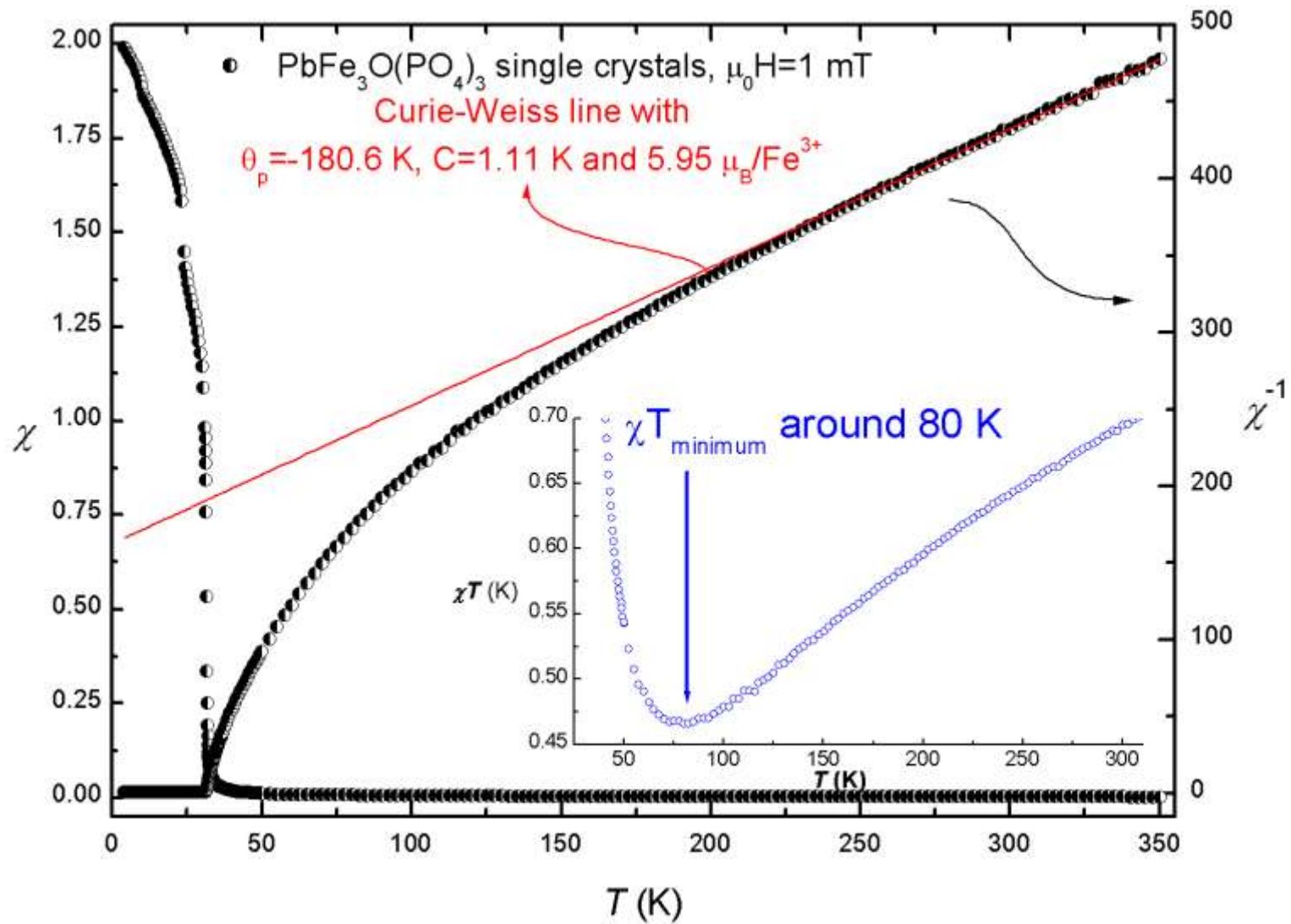


Planes are connected by $[\text{PO}_4]$ tetrahedra. Pb^{2+} cations occupy cavities located between these planes

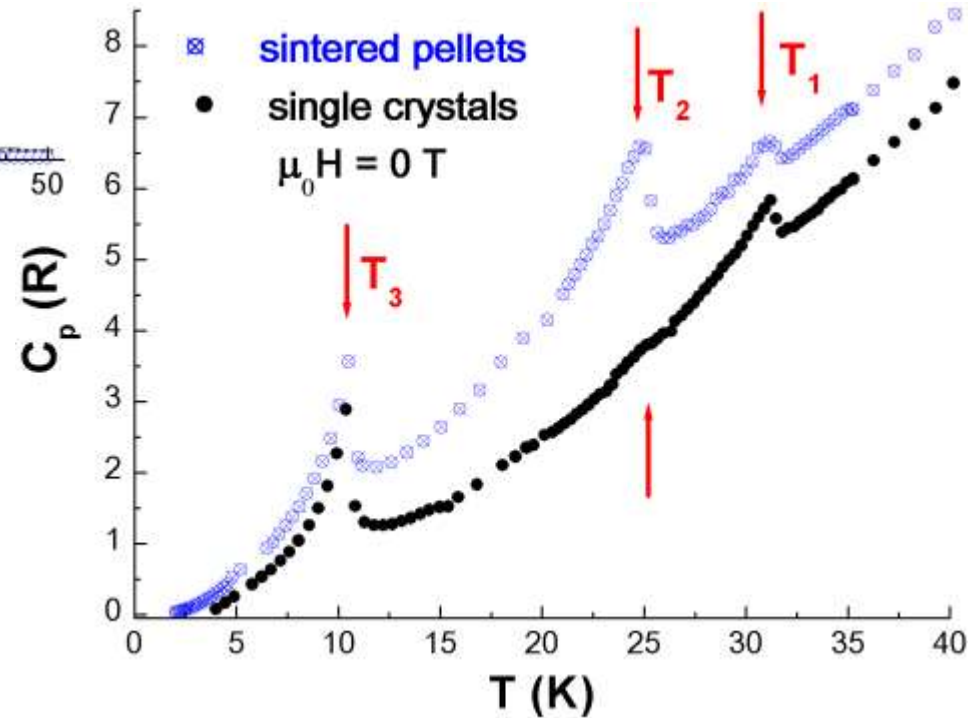
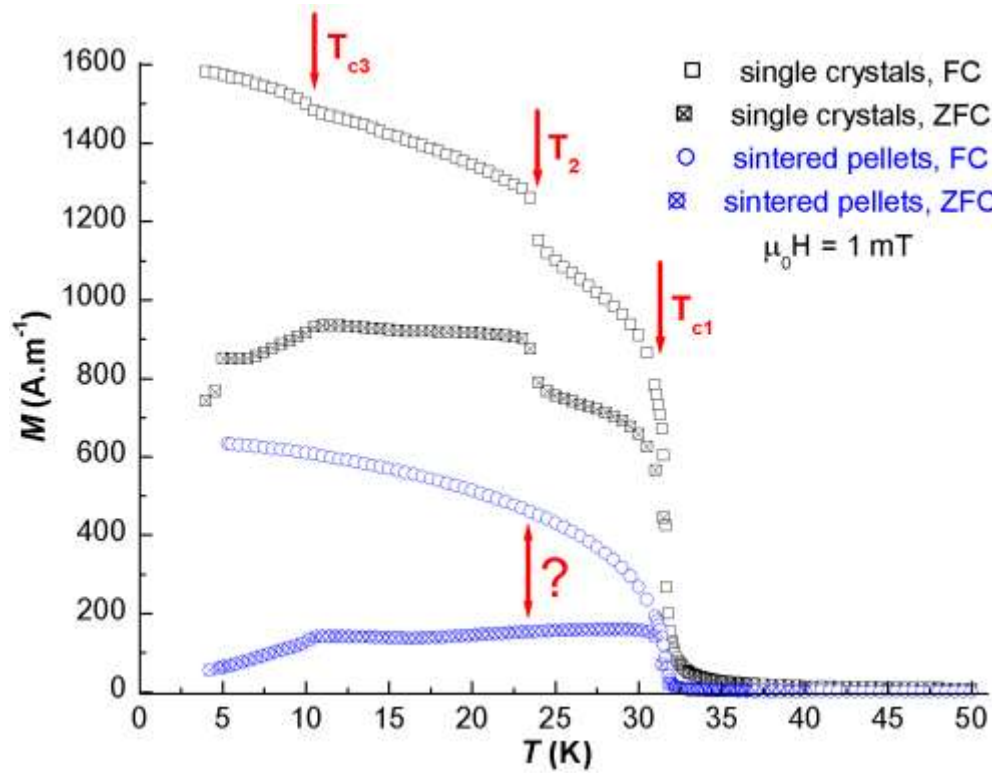


3D framework showing channels along the b direction

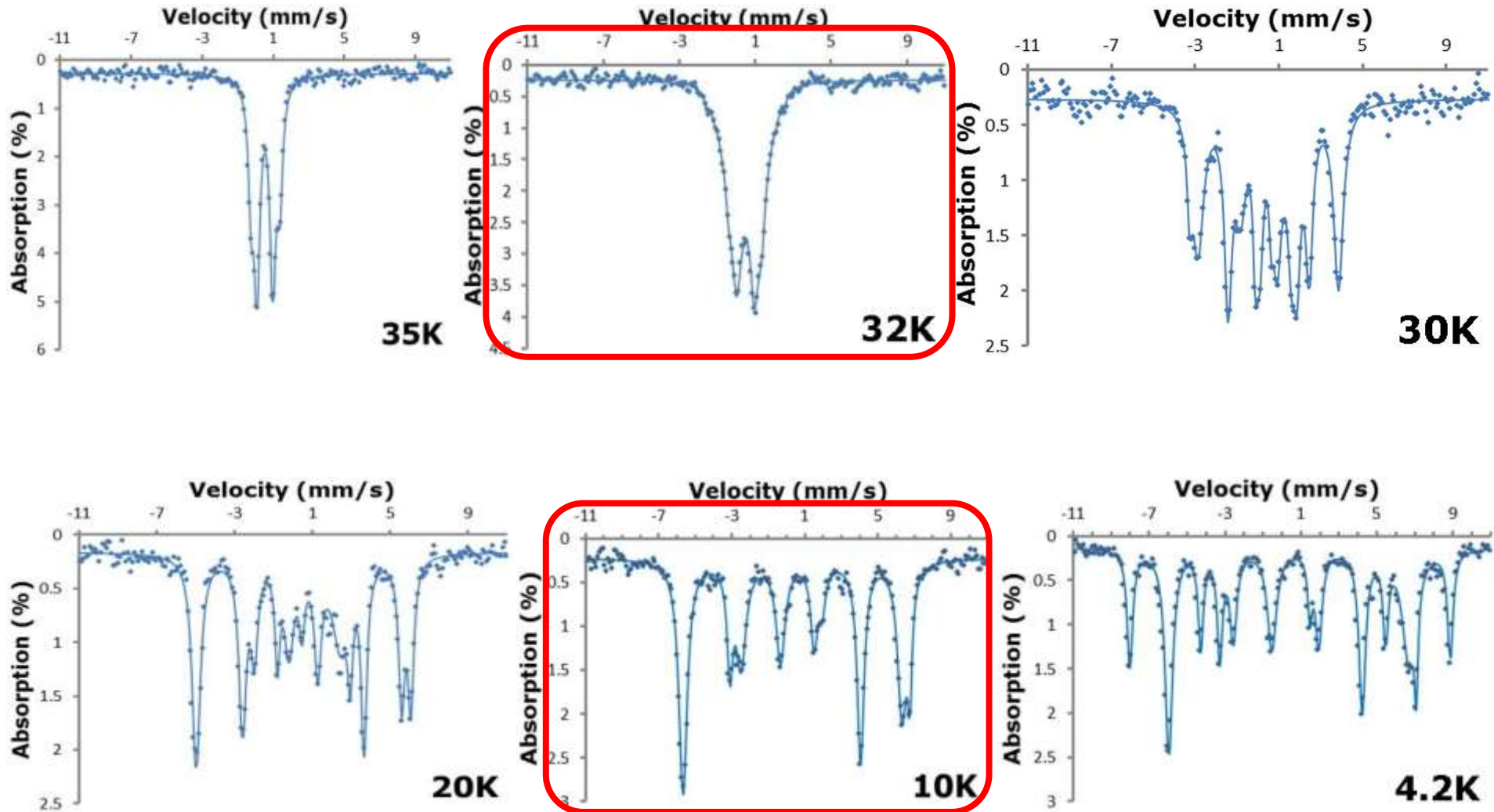
Static susceptibility measurements



Comparison of thermodynamic response functions in both $\text{PbFe}_3\text{O}(\text{PO}_4)_3$ single crystals and sintered pellets



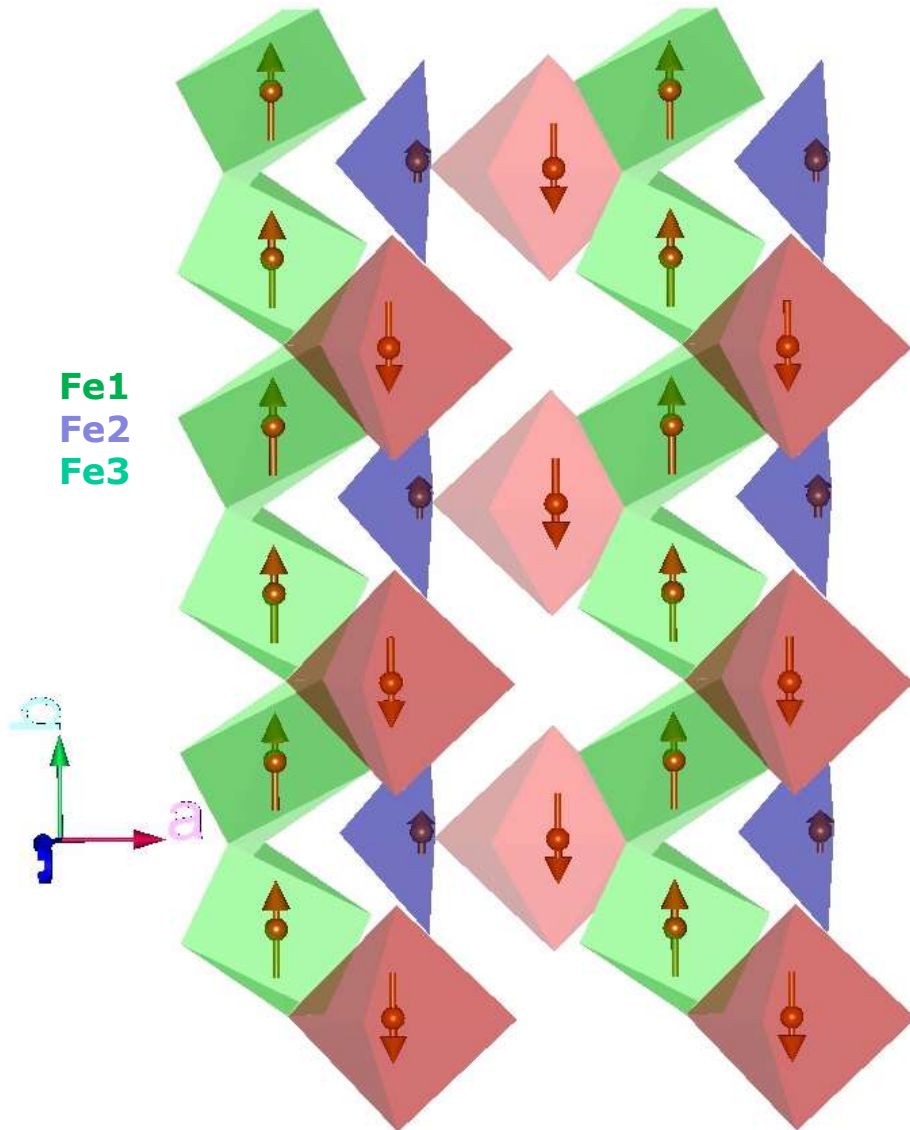
$\text{PbFe}_3\text{O}(\text{PO}_4)_3$: Mössbauer study



Purely magnetic and temperature reversible phase transition at 32 and 10 K

Magnetic structure of $\text{PbFe}_3\text{O}(\text{PO}_4)_3$ at 30 K

(single crystal neutron scattering, Collaboration With G. Nénert, ILL, Grenoble)



All magnetic moments are practically lined up parallel to b direction

Monophosphates



Crystalline and vitreous materials

Synthesis :

Glasses : Melting + quenching

Powder: crystallisation of glasses. solid state reaction.

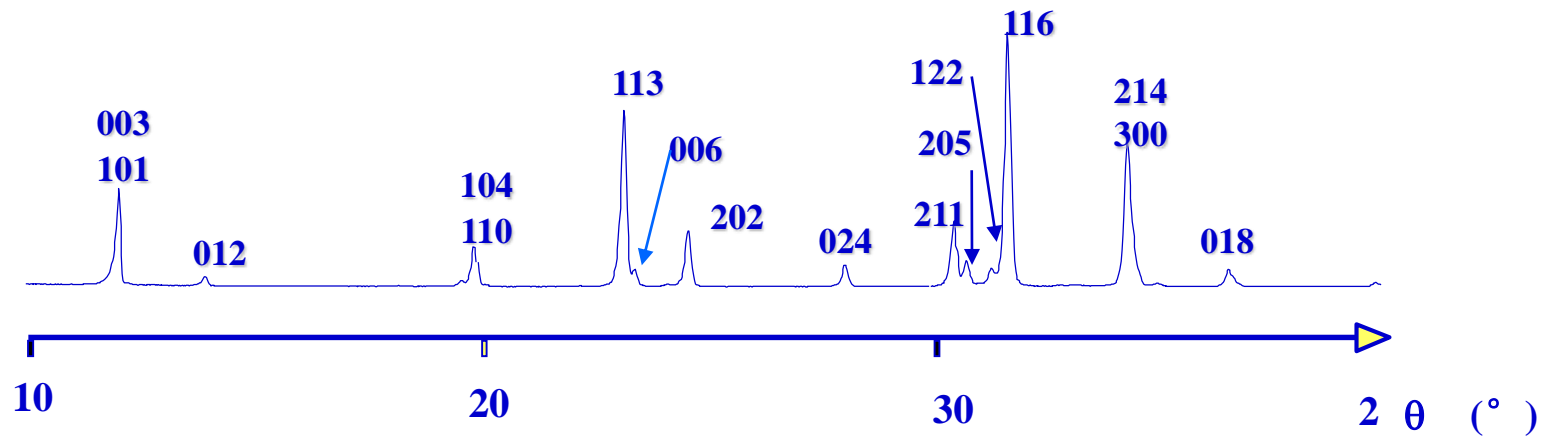
Single crystals : Melting + slow cooling

Characterizations :

XRD, DTA, Density, Raman, UV-VIS, Ionic conductivity,
Bioactivity

Crystalline phases

XRD : $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ (Nasicon)



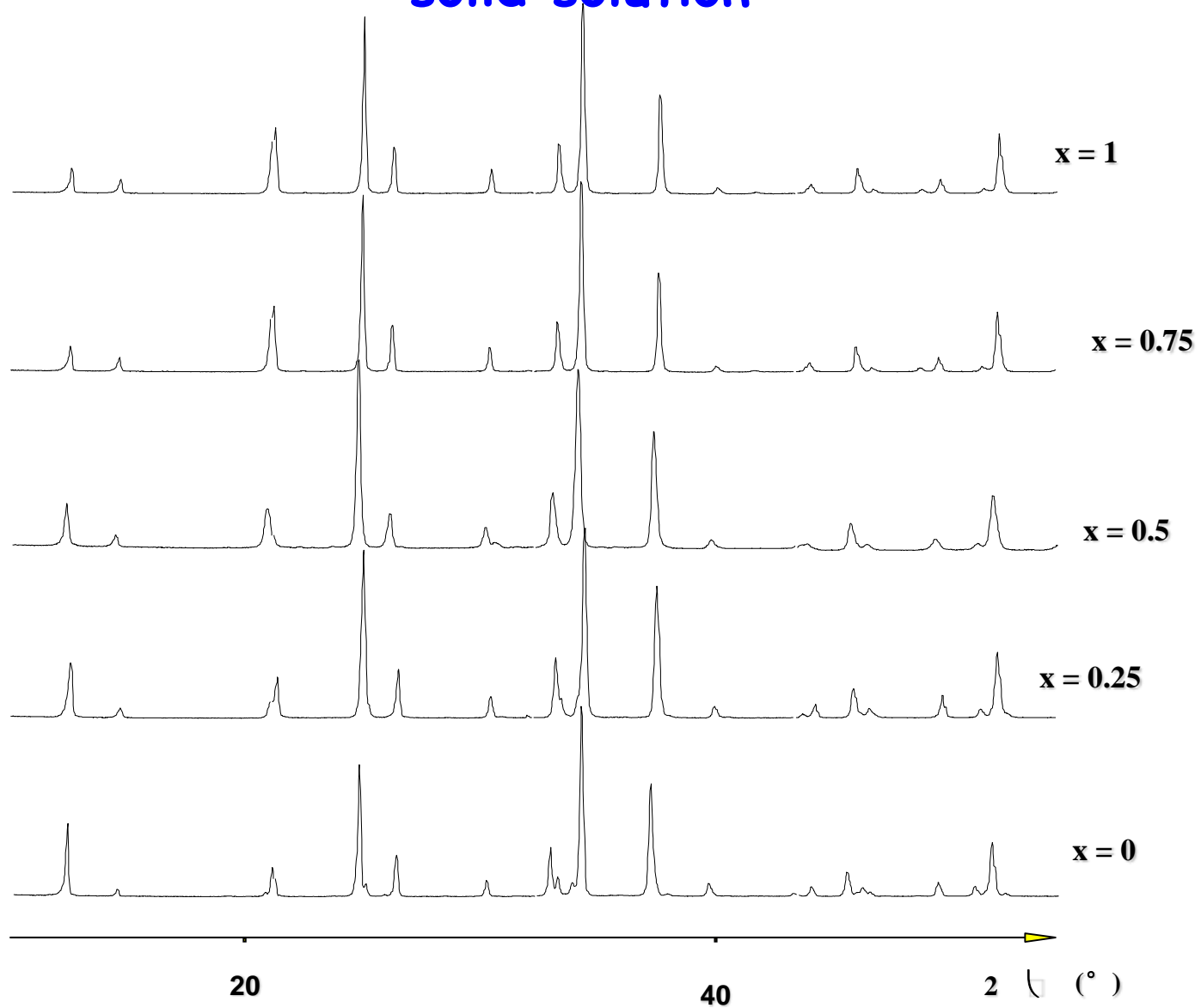
Cell parameters

Hexagonal, S. G. : R32

$$a_h = 9.061 \text{ \AA} \quad c_h = 21.734 \text{ \AA}$$

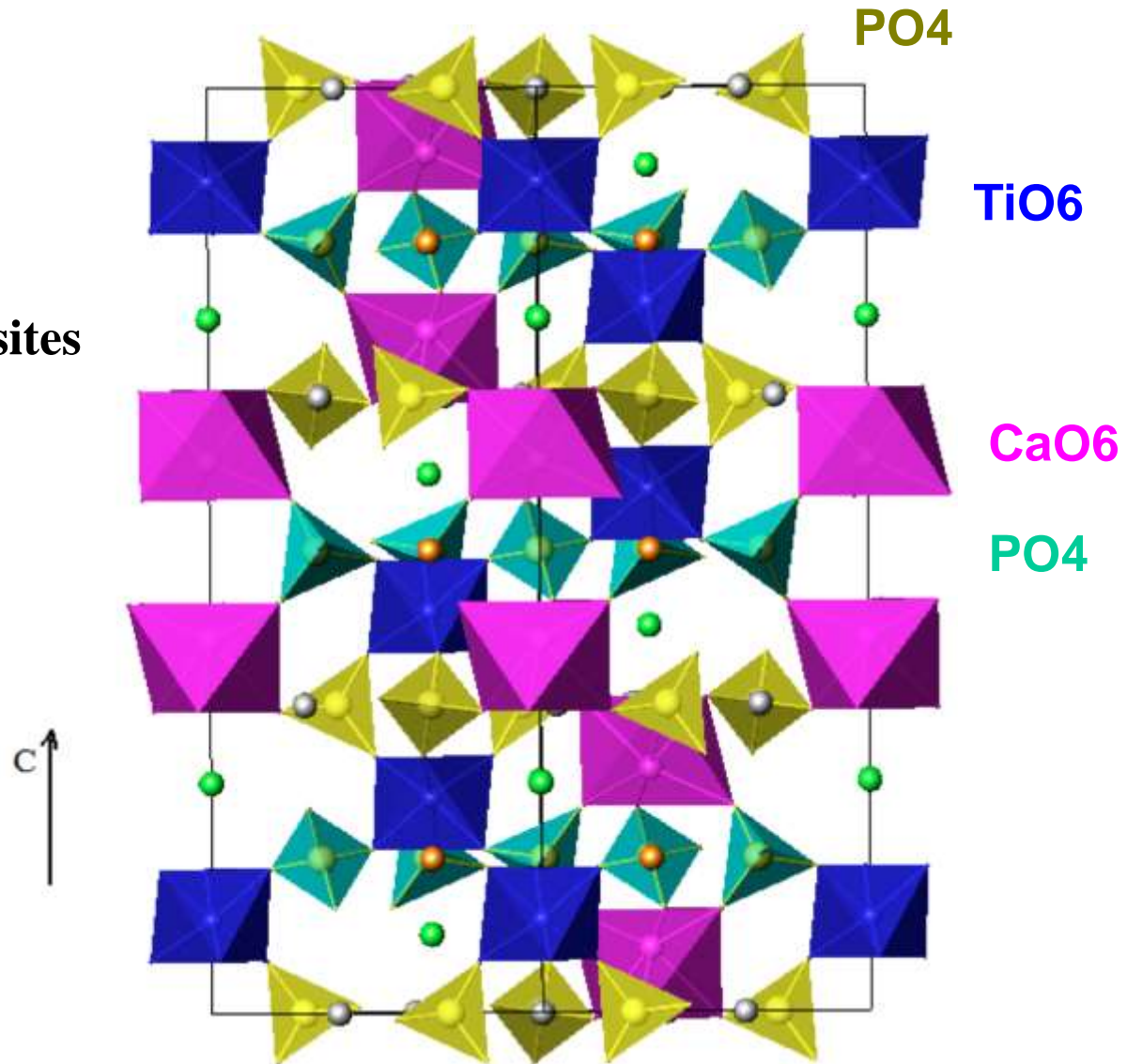


solid solution

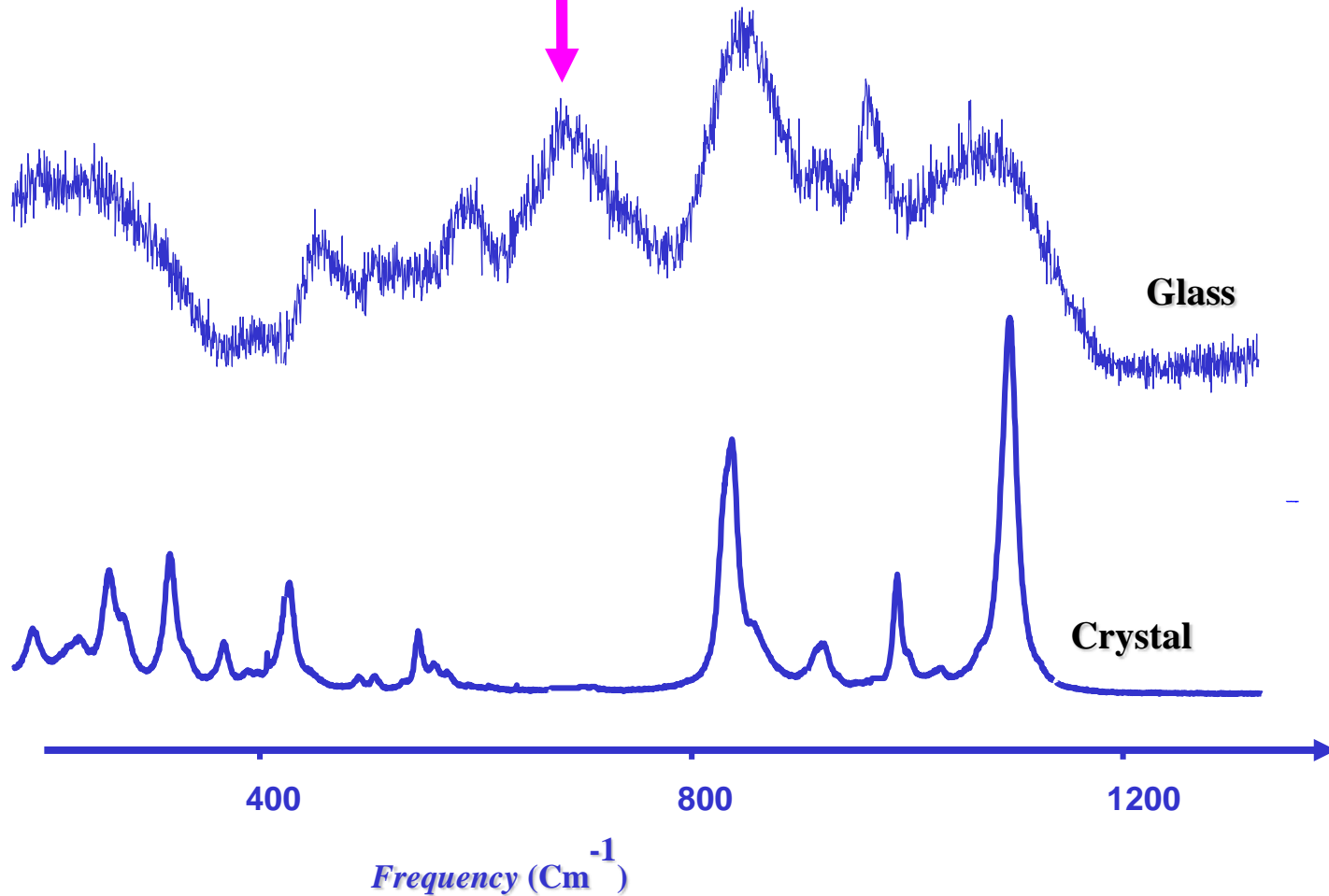


Structure of $\text{Na}_3\text{CaTi}(\text{PO}_4)_3$

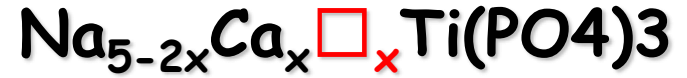
Na : M1 and M2 sites



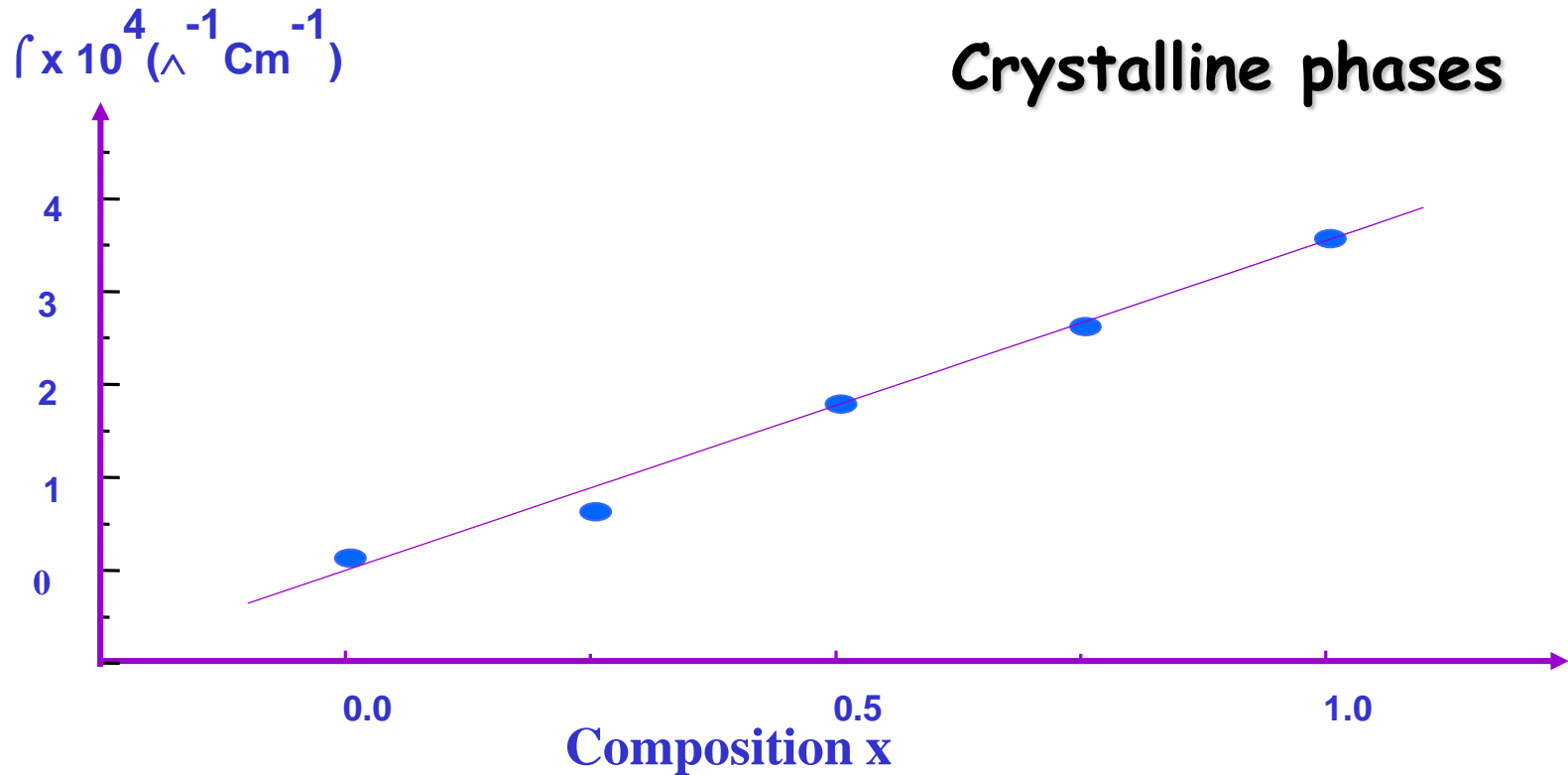
Raman



Ionic Conductivity at 300° C



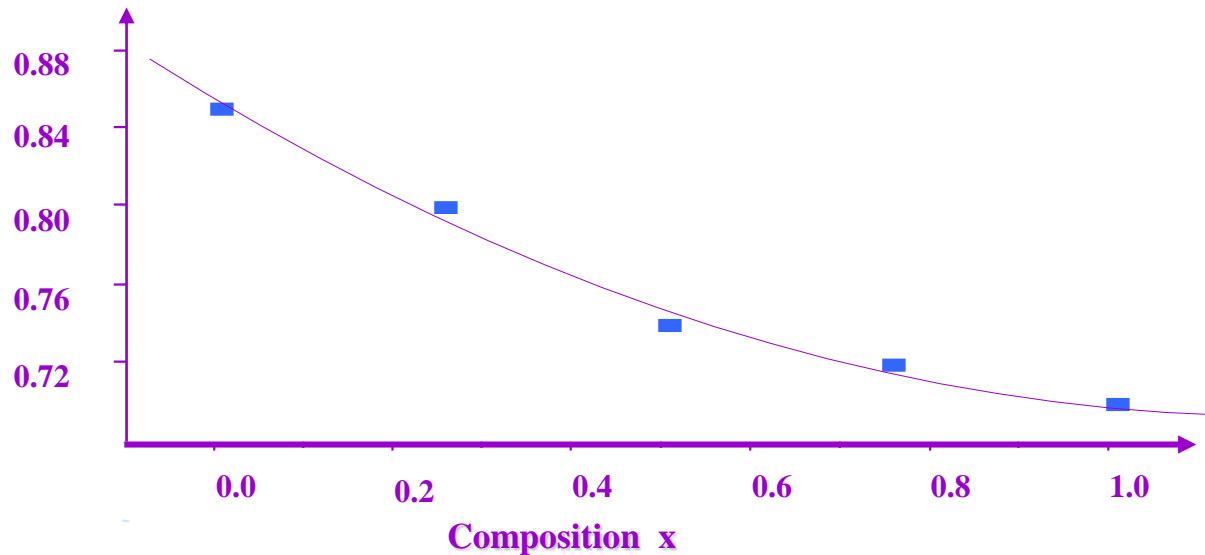
Crystalline phases



Activation energy

$\text{Na}_{5-2x}\text{Ca}_x\text{Ti}(\text{PO}_4)_3$ crystalline phases

E_a (eV)



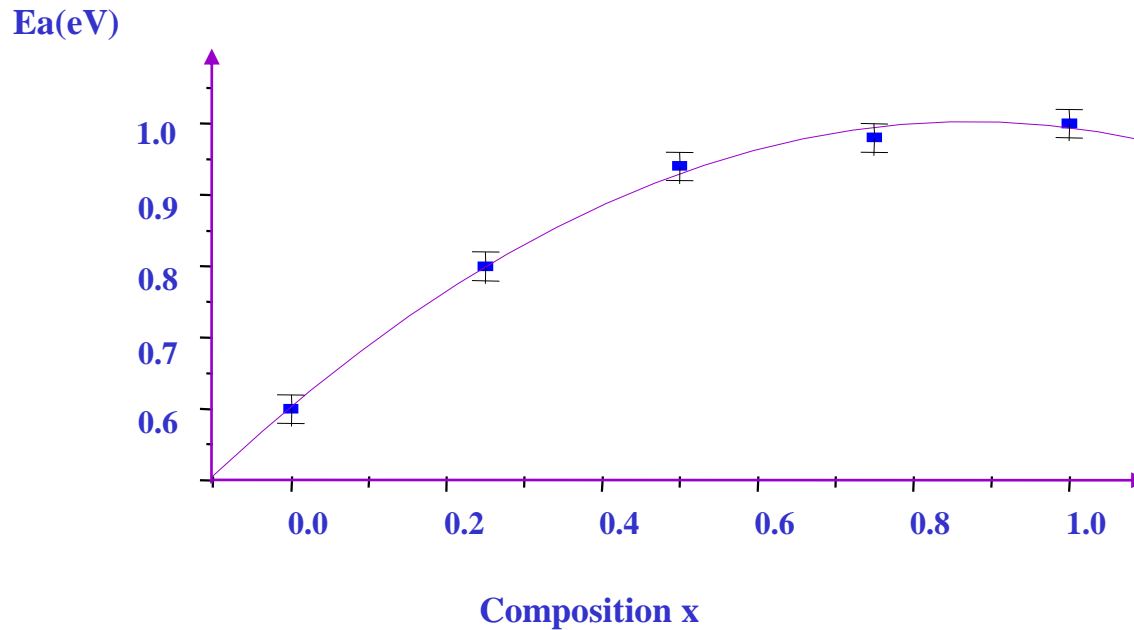
☞ Empty sites (vacancies)

☞ A^{2+} (Ca^{2+}) in [A] sites (framework)

Displacement of Na^+ ions is facilitated

Activation energy

$\text{Na}(5-2x)\text{Ca}_x\text{Ti}(\text{PO}_4)_3$ glasses



Replacement of Na^+ ions by Ca^{2+}



**Bioglasses
Cell Culture**

**Tests of human cells, isolated from human
bone marrow**

$\text{Na}_{5-2x}\text{Ca}_x\text{Ti}(\text{PO}_4)_3$: Bioglasses



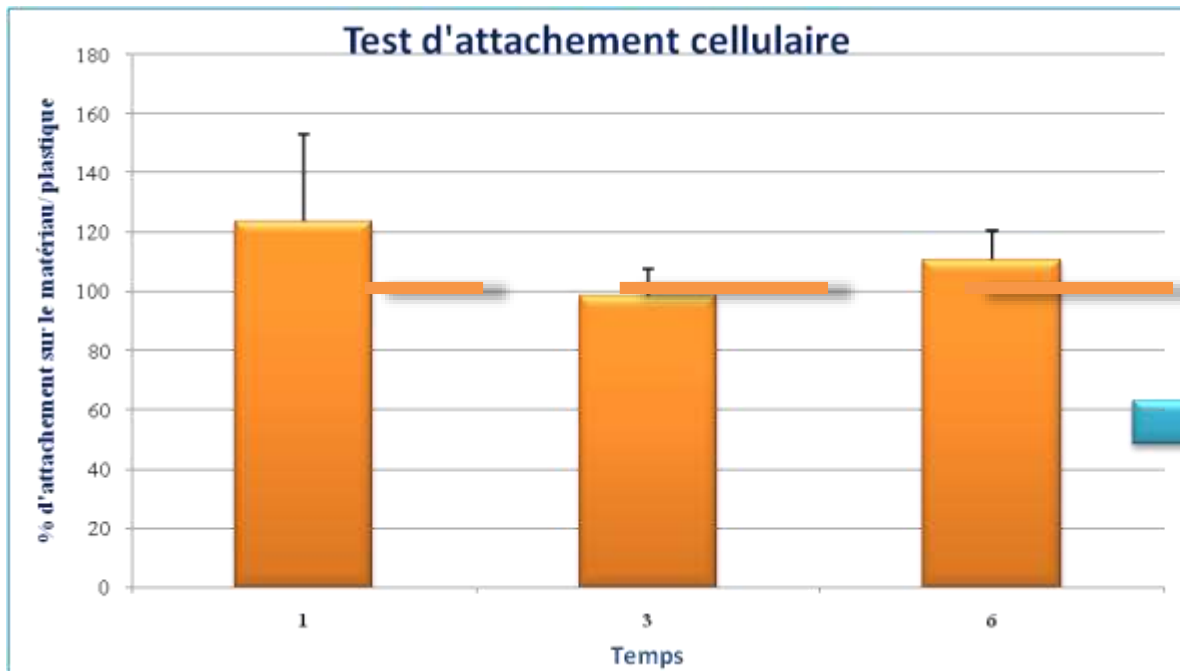
Guenching



Glass bars are cut. The pellets are used for bioactivity tests

IN VITRO TESTS

Attachment test with HBMSC (Human Bone Marrow Stromal Cells)



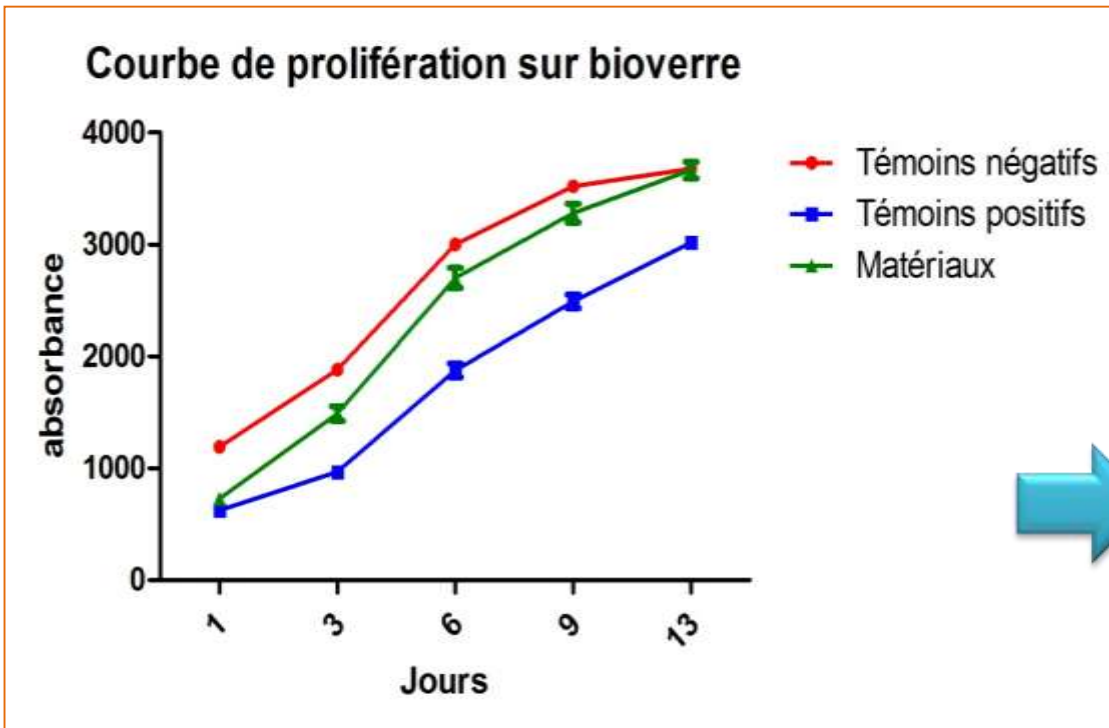
Plastic
100% Attachment



Very good attachment
on bioglass compared
to plastic.

Proliferation test with HBMSC

Periods : 1, 3, 6, 9 and 13 days



Very good growth of cells on bioglasses

IN VIVO TESTS



Anesthesia of the rats



Preparation of the surgical area and isolation of the bone



Creation of the implantation site

Implantation of the glass

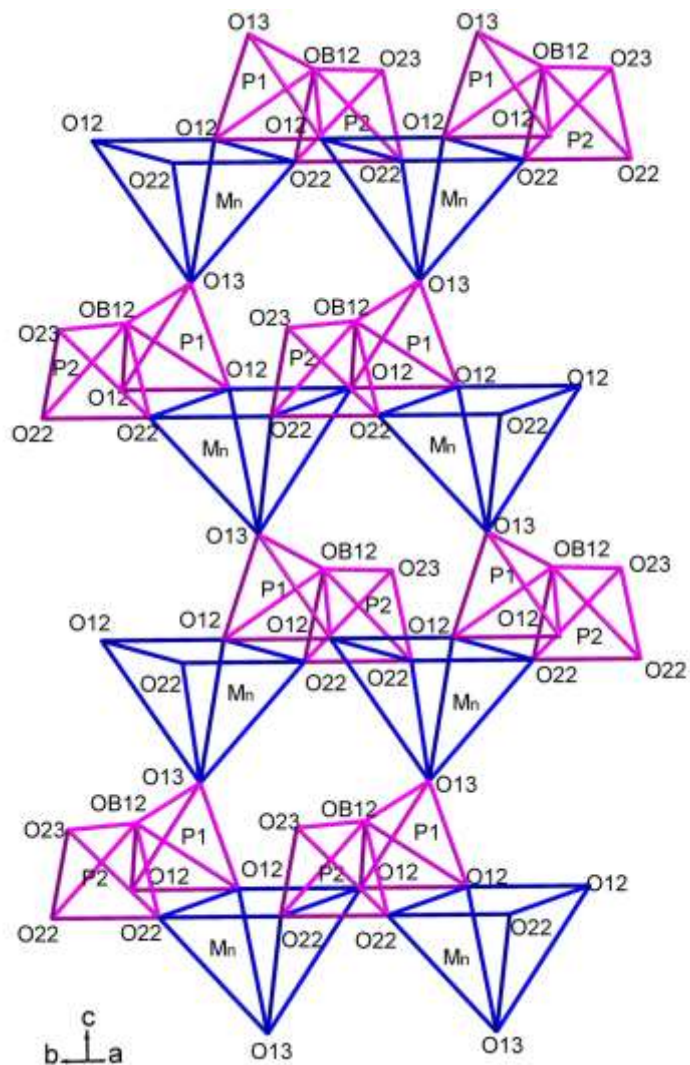


Rearrangement of the area

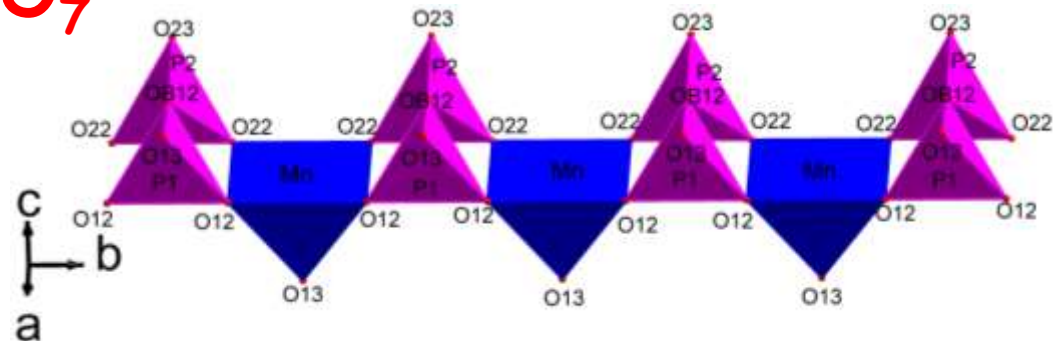
Histological study



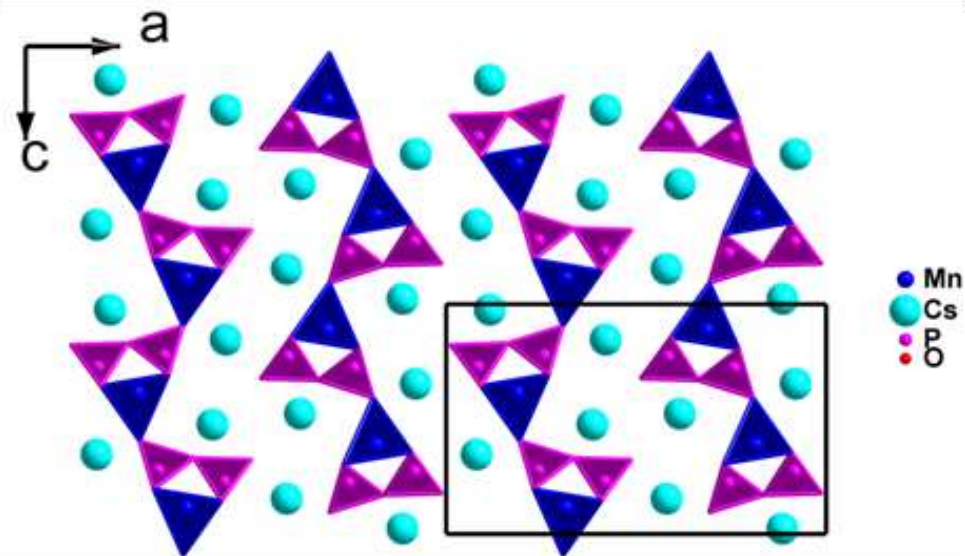
Diphosphate: $\text{Cs}_2\text{MnP}_2\text{O}_7$



Connexion of $[\text{MnOP}_2\text{O}_7]_\infty$ chains by O13 to form sheets parallel to (b,c) plane

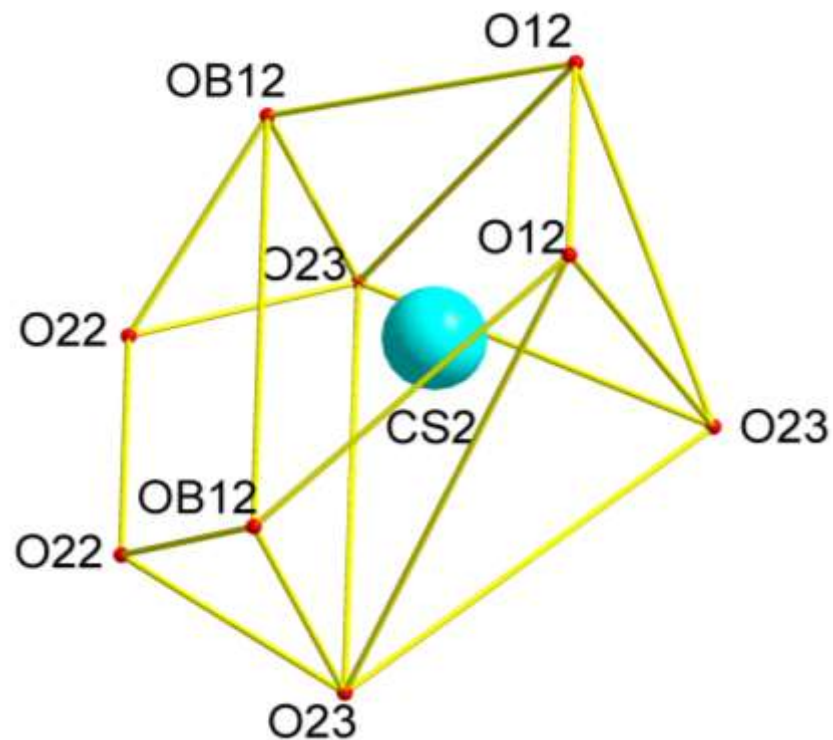
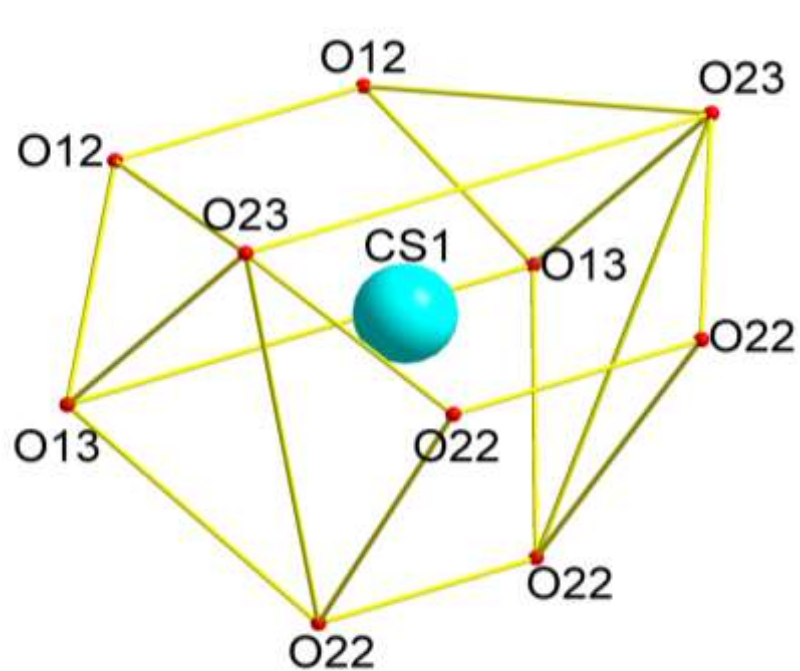


MnO_5 and P_2O_7 groups form infinite chains $[\text{MnOP}_2\text{O}_7]_\infty$, along b axis.



Projection on (a,c) plane

Cesium atoms are located between the sheets in two sites, 9-fold and 10-fold coordination



Cesium polyhedra in $\text{Cs}_2\text{MnP}_2\text{O}_7$

Cesium atoms are located between the sheets
in two sites nine fold + ten fold coordination

Summary

Phosphates exist in both crystalline and vitreous forms

Numerous and diverse crystal structures

Structures of phosphates accommodate all most of the periodic table elements

Numerous properties

Energetical, medical and environmental applications

Acknowledgements

Casablanca : Saida Kaoua, Saida Krimi, Samiha Lamrhari,

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Stanislav Pechev, Matias Velazquez,
Hassan El hafid, Joelle Amédée

Pretoria : Danita de Waal

Wake Forest : Abdou Lachgar, Cinthya Day

Thank you for your attention

