# Mixed anions (F, O, H, S) compounds : synthesis, structures and electronic, magnetic, optical properties

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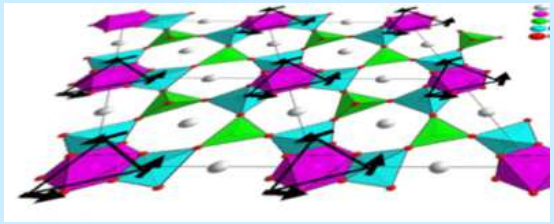


GDR MEETICC

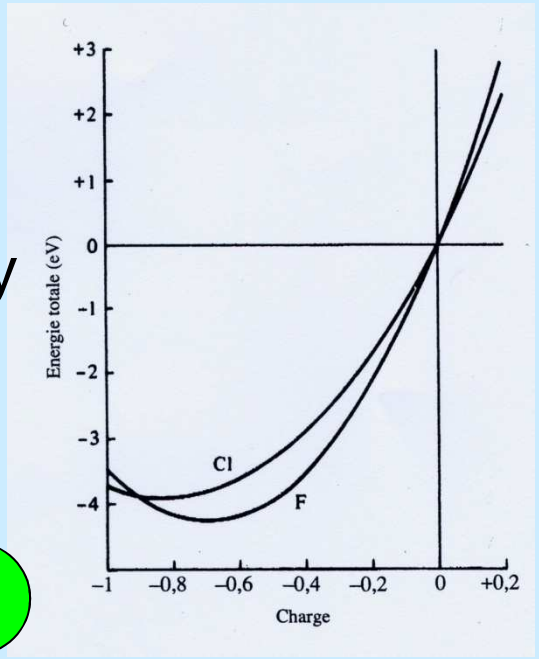
**Matériaux, Etats ElecTronIques et Couplages non-Conventionnels**

4-10 Février 2018, Banyuls

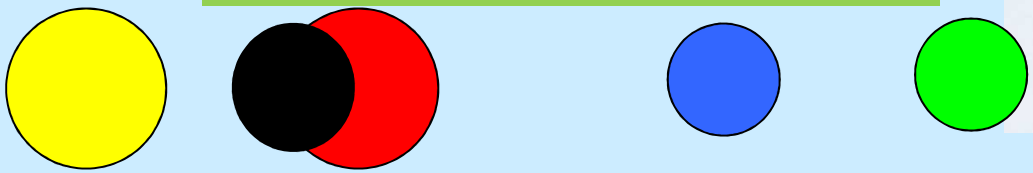
$E(q) = \alpha q + \beta q^2$ **Mulliken**-Jaffé (1935 – 1963)

$\chi(q) = \delta E(q)/\delta q = \alpha + 2\beta q$ : Electronegativity

$\eta = \delta^2 E(q)/\delta^2 q = 2\beta$ : Hardness= 1/Polarizability (Pearson)



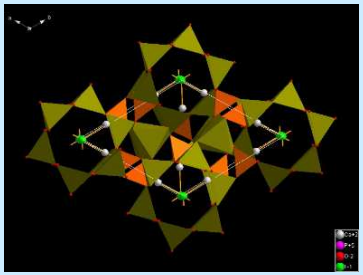

# The anions $X^{p-}$



$\chi(q)$ — $S^{2-}$ — $N^{3-}$ $Cl^-$ — $O^{2-}$ — $F^-$ → + electronegative

$H^{\delta-}$ $OH^-$

* (Green apatites) $H^- + O^{2-} \leftrightarrow 2e^- + OH^-$



Apatite : $Ca_5(PO_4)_3$(**F, OH, H**)

$\eta$ — $S^{2-}$ — $N^{3-}$ — $Cl^-$ — $O^{2-}$ — $F^-$ → + hard

+ polarizable

* K. Hayashi and H. Hosono, J. Phys. Chem. Chem. Phys, 2016, 18, 323, 8186-8195

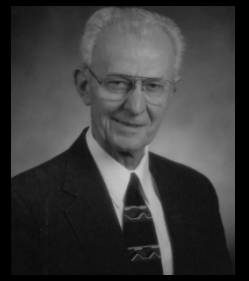
# Pauling electronegativity $\chi$


1929 (Rules), 1954 (Nobel Prize),
1962 (Nobel peace prize)

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,2 H 1 | | | | | | | | | | | | | | | | | He 2 |
| 0,98 Li 3 | 1,57 Be 4 | | | | | | | | | | | 2,04 B 5 | 2,55 C 6 | 3,04 N 7 | 3,44 O 8 | 3,98 F 9 | Ne 10 |
| 0,93 Na 11 | 1,31 Mg 12 | | | | | | | | | | | 1,61 Al 13 | 1,9 Si 14 | 2,19 P 15 | 2,58 S 16 | 3,16 Cl 17 | Ar 18 |
| 0,82 K 19 | 1 Ca 20 | 1,36 Sc 21 | 1,54 Ti 22 | 1,63 V 23 | 1,66 Cr 24 | 1,55 Mn 25 | 1,83 Fe 26 | 1,88 Co 27 | 1,91 Ni 28 | 1,9 Cu 29 | 1,65 Zn 30 | 1,81 Ga 31 | 2,01 Ge 32 | 2,18 As 33 | 2,55 Se 34 | 2,96 Br 35 | Kr 36 |
| 0,82 Rb 37 | 0,95 Sr 38 | 1,22 Y 39 | 1,33 Zr 40 | 1,6 Nb 41 | 2,16 Mo 42 | 2,1 Tc 43 | 2,2 Ru 44 | 2,28 Rh 45 | 2,2 Pd 46 | 1,93 Ag 47 | 1,69 Cd 48 | 1,78 In 49 | 1,96 Sn 50 | 2,05 Sb 51 | 2,1 Te 52 | 2,66 I 53 | Xe 54 |
| 0,79 Cs 55 | 0,89 Ba 56 | 1,1 La 57 | 1,3 Hf 72 | 1,5 Ta 73 | 1,7 W 74 | 1,9 Re 75 | 2,2 Os 76 | 2,2 Ir 77 | 2,2 Pt 78 | 2,4 Au 79 | 1,9 Hg 80 | 1,8 Tl 81 | 1,8 Pb 82 | 1,9 Bi 83 | 2 Po 84 | 2,2 At 55 | Rn 86 |
| 0,7 Fr 87 | 0,9 Ra 88 | 1,1 Ac 89 | Rf 104 | Db 105 | Sg 106 | Bh 107 | Hs 108 | Mt 109 | Ds 110 | Rg 111 | Cn 112 | 113 | 114 | 115 | 116 | 117 | 118 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,12 Ce 58 | 1,13 Pr 59 | 1,14 Nd 60 | 1,13 Pm 61 | 1,17 Sm 62 | 1,2 Eu 63 | 1,2 Gd 64 | 1,2 Tb 65 | 1,22 Dy 66 | 1,23 Ho 67 | 1,24 Er 68 | 1,25 Tm 69 | 1,1 Yb 70 | 1,27 Lu 71 |
| 1,3 Th 90 | 1,5 Pa 91 | 1,7 U 92 | 1,3 Np 93 | 1,3 Pu 94 | 1,3 Am 95 | 1,3 Cm 96 | 1,3 Bk 97 | 1,3 Cf 98 | 1,3 Es 99 | 1,3 Fm 100 | 1,3 Md 101 | 1,3 No 102 | 1,3 Lr 104 |

Hard-Soft Acid-Base (**HSAB**) theory
Ralph Pearson (1960)



*Energy*

Hard acid : $H^+(1s^0)$, $Ti^{4+}(3d^0)$, $K^+$, $Ba^{2+}$, $La^{3+}$

Soft acid : $Fe^{2+}(3d^6)$, $Cu^+(3d^{10})$

---

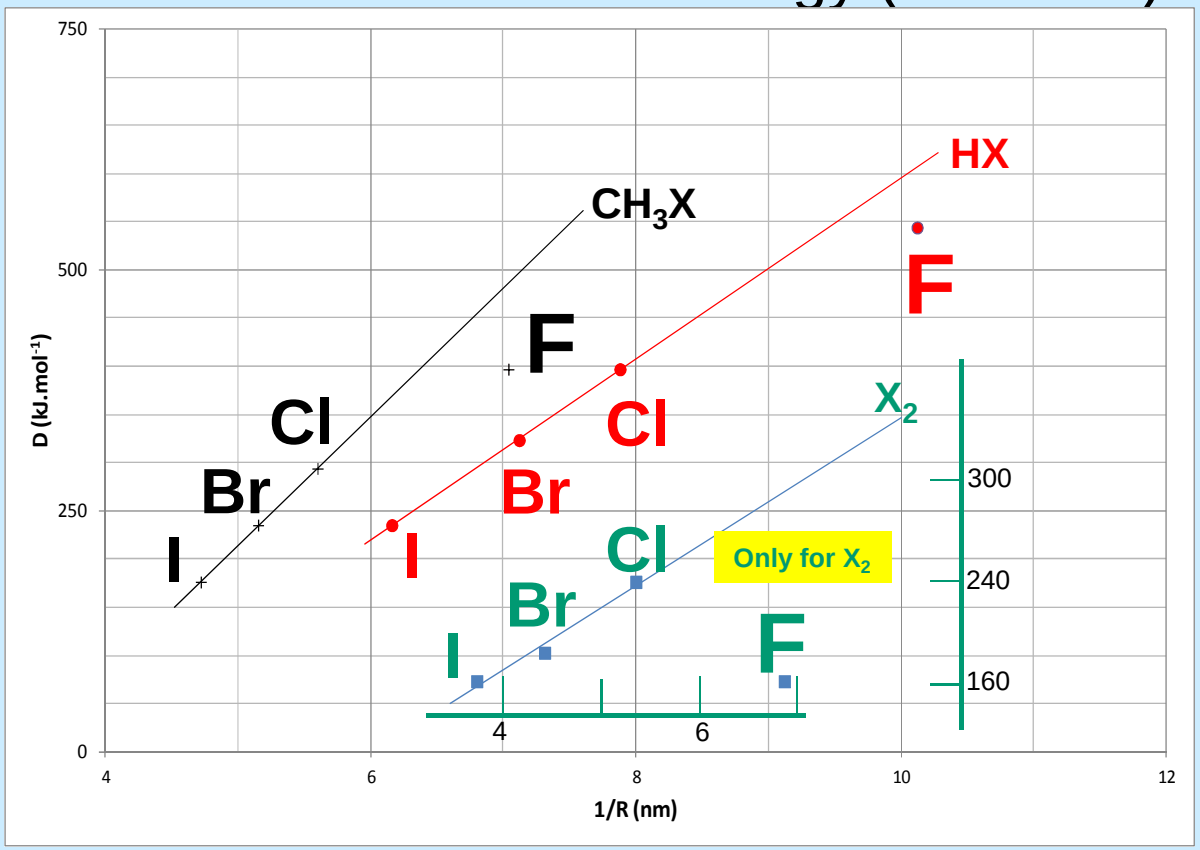
Soft base : $H^-(1s^2)$, $S^{2-}$, $I^-$, $SO_4^{2-}$, $CO_3^{2-}$

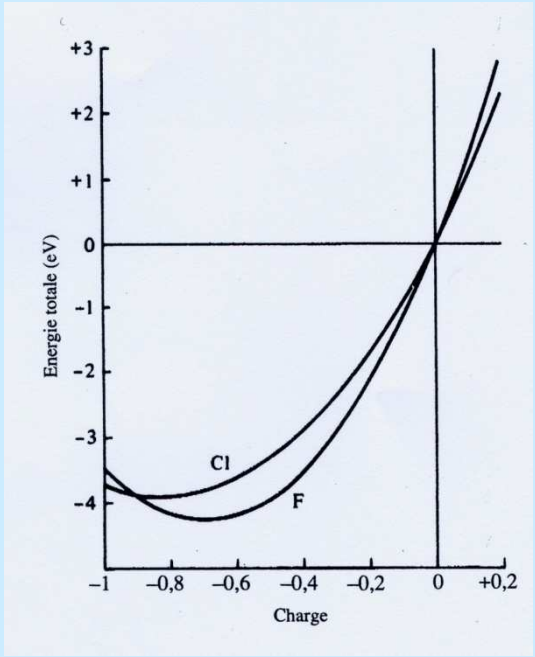
Hard base : $F^-$, $O^{2-}$, $OH^-$, $Cl^-$, $NH_3$

Hard-Hard or Soft-Soft AB react faster leading to stronger bonds !

# Fluorine, a super-halogen !
# The anomolous properties of Fluorine

## Bond-Dissociation Energy (kJ.mol-1)




$F^-$

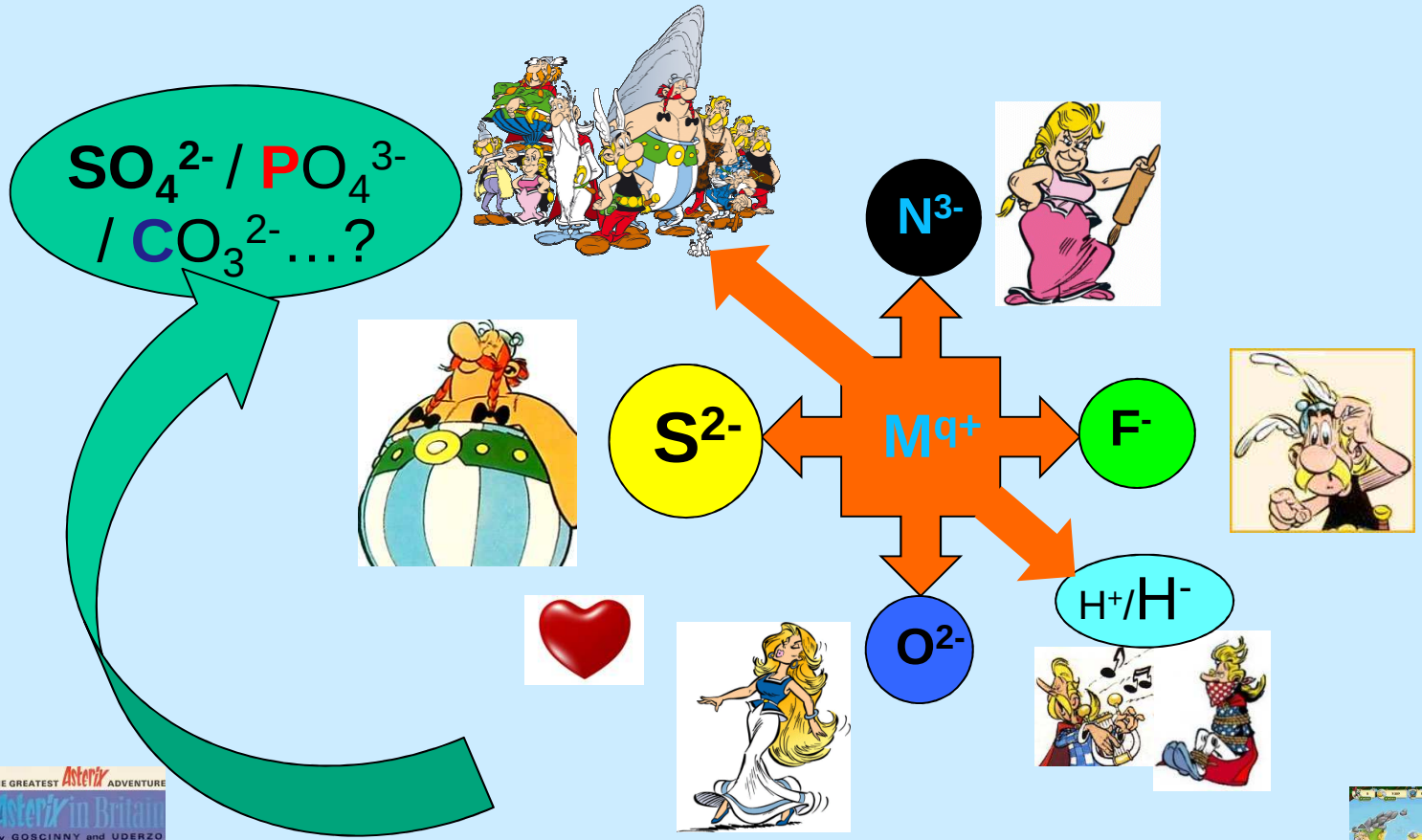
Fluorine is small in size and its supported charge is too high !

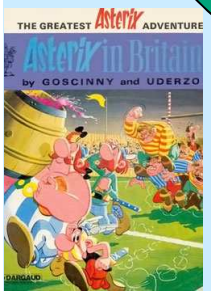
# The M-X chemical bonding and the effect of mixed anions

$M^{q+}$ : Partial density of charges and oxydation states

Point group ( $M^{q+}$ / $X^{p-}$ ), anisotropy and networks

Crystal field, Polarization, Covalency



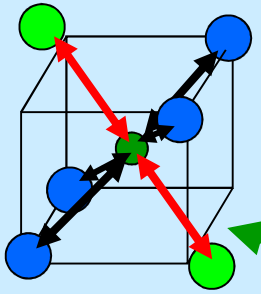




A way to tune the ionicity-covalency of the chemical bonding and consequently the electronic properties !

## Outline

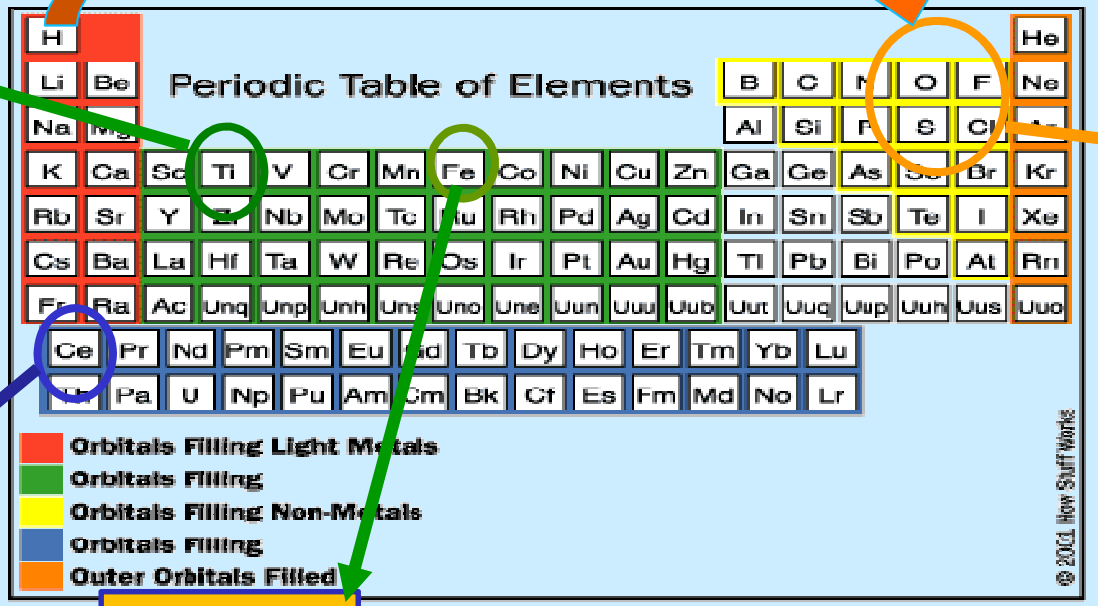
***Rare-Earth (Ce) and Transition Metal (Ti, Fe) mixed anions (F, O, S, H) compounds***
***Composition, Structural features and Energy Gap***

# *From 2D layers to 3D tunnel networks*

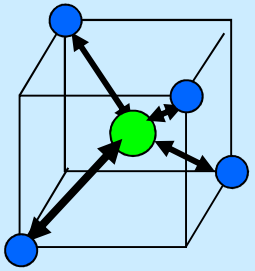


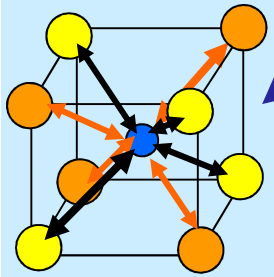
$Ti^{4+}(J=0)/Ti^{3+}(J=3/2)$

**$^{22}$Ti**
Pauling : 1.4
[Ar] $4s^2 3d^2$




$H^-$ $OH^-$ $O^{2-}$ $F^-$ $S^{2-}$

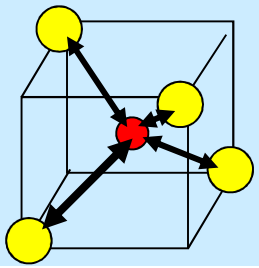




$Ce^{4+}(J=0)/Ce^{3+}(J=5/2)$

**$^{58}$Ce**
Pauling : 1.1
[Xe] $6s^2 4f^2$

**$^{26}$Fe**
Pauling : 1.8
[Ar] $4s^2 3d^6$



$Fe^{2+}$ ($^5T_2$)

The key role of Electronegativity ($\chi$), Charge ($Z^+$), Ionic radius ($r_{ion}$) of $M^{z+}$ to define local electrical field = $\chi(Z)/ r_{ion}$

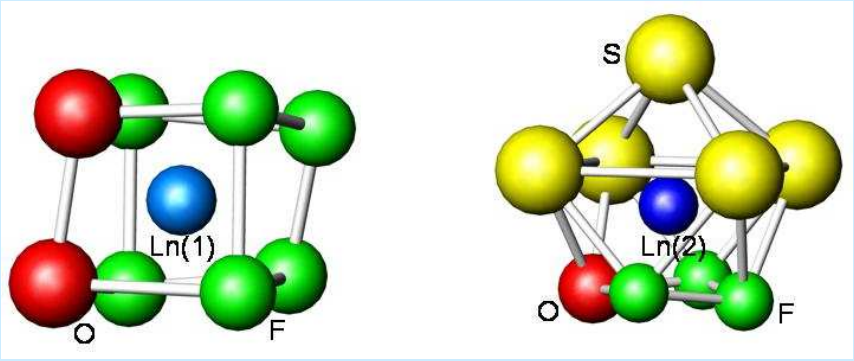
***Point group symmetry (M vs X),***
Mixing empty d orbitals with filled ligand p orbitals
Looking for non-bonding character
Lowering the band gap

## *The mixed anions systems : absorption k(λ) and refractive index n(λ)*

***- Electronegativity ↓ (Polarizability ↑) : $F^-$ > $O^{2-}$ > $S^{2-}$***

| | $LaF_3$ | $La_2O_3$ | $\gamma$-$La_2S_3$ |
|---|---|---|---|
| $\lambda_{abs}$ | 175 nm | 230 nm | 440 nm |
| n(400 nm) | 1.8 | 2.1 | 2.7 |

***- Modulation of the chemical bond : Ln-S/O/F : Variation of the absorption wavelength and refractive index***

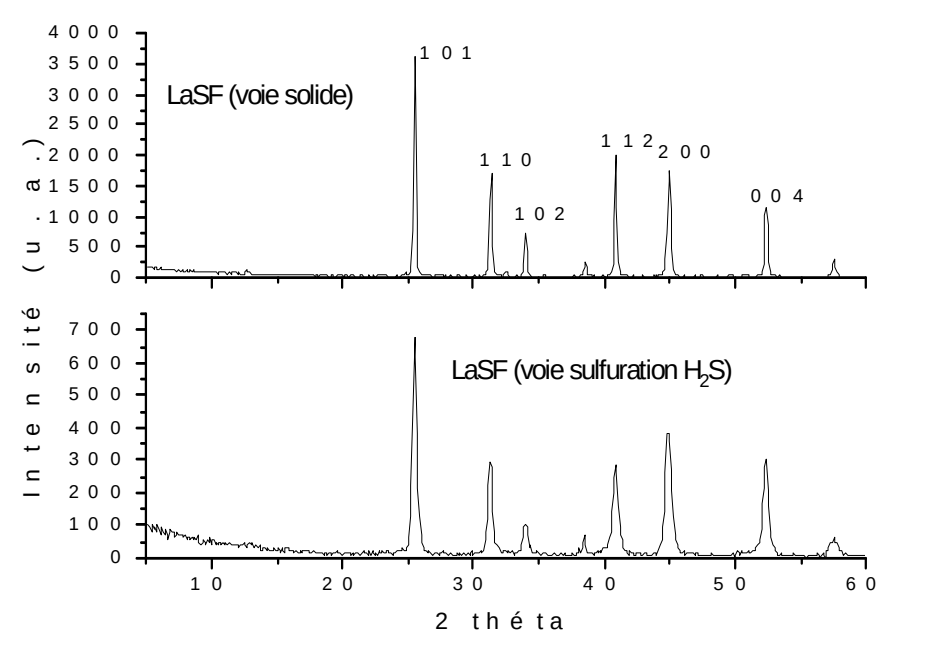


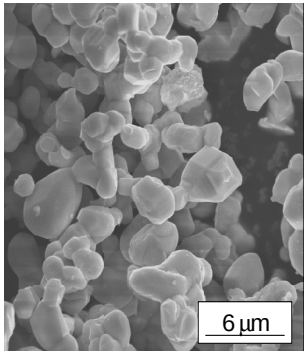

***- Competitive bonds around metals : anisotropy, modification of the chemical bonds and electronic properties***

# *(F, O ,S) compounds synthesis routes*

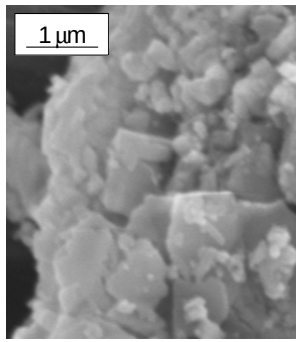
***Solid state route*** *: $LnF_3 + Ln_2O_3 + Ln_2S_3$ (stoichiometric mixture)*
*Sealed quartz tube, Pt crucible , T = 900°C - 1100°C*

***Preparation from oxyfluorides or fluorocarbonates***
*(precipitation of salts and annealing)*
*$LnOF\ (LnFCO_3) \rightarrow LnSF(O)$ ( T = 500°C- 600°C, $H_2S$-$CS_2$-Ar)*




Voie solide



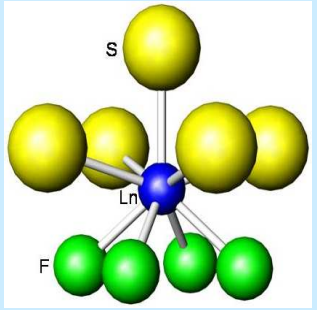

Voie sulfuration

## *A new class of compounds : rare earth oxyfluorosulfides*

LaSF : $\lambda_{abs}$ = 440 nm (Eg = 2.8 eV)
High absorption efficiency and refractive index

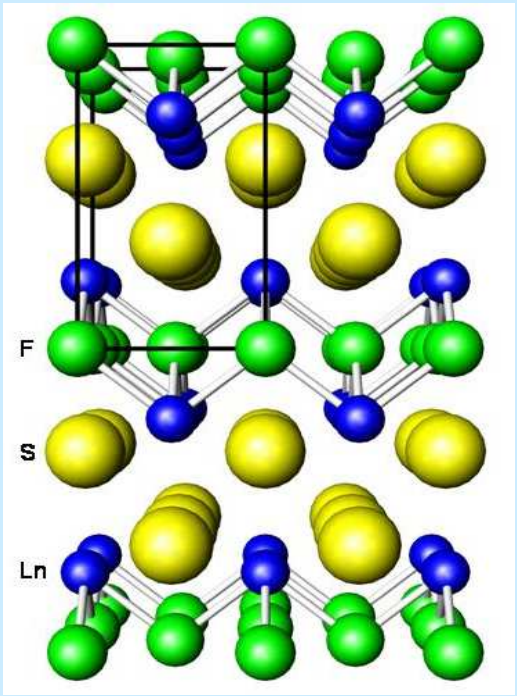
UV Absorbers : $\lambda_{abs}$ = 400 nm (Eg = 3.1 eV) ??

Modification of rare earth environment




V/ZX= 28.6 $A^3$ (S.Andersson)

Electrostatic valence (Pauling) :
S(-1.66) + F (-1.33)= - 3




Intergrowth of

Ionic blocks $[Ln_2F_2]^{4+}$

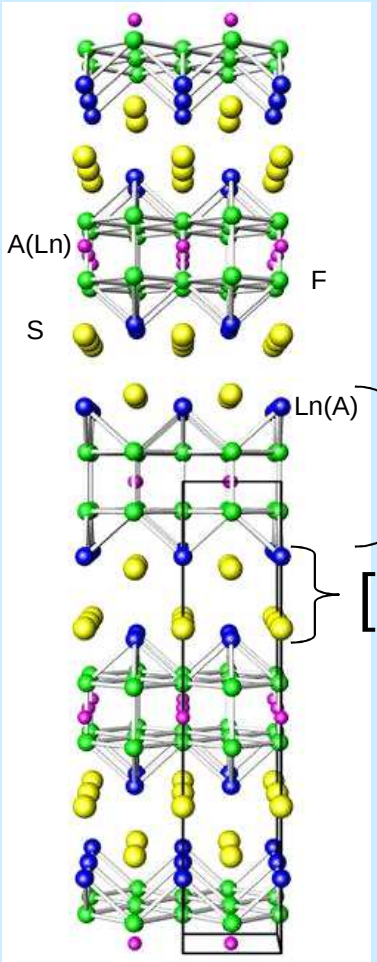
Covalent blocks $[S_2]^{4-}$

How to change the ionicity of blocks ?

Size
+
Charge

# *A new class of compounds : rare earth oxyfluorosulfides*

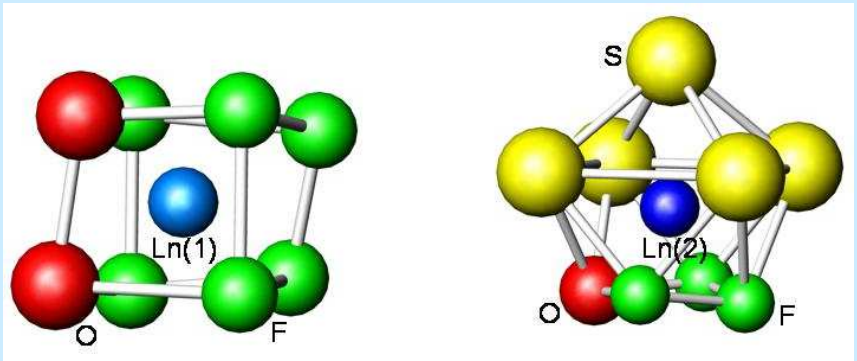
**Modification of the size (ionicity) of '[Ln-O,F]' blocks : double sulphur sheets**

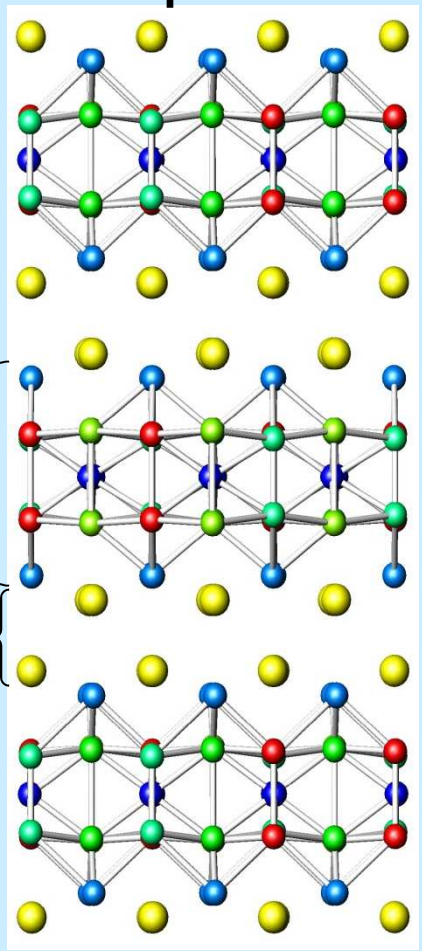



$[Ln_2AF_4]^{4+}$

$[S_2]^{4-}$

**Powder and Single crystal X-Ray and Electron Diffraction analysis**



$[Ln_3OF_4]^{4+}$

$[S_2]^{4-}$

2 LnSF + $AF_2$

$Ln_2AF_4S_2$ (A= Ca, Sr)

Tetragonal I4/mmm

a ≈ 4 Å, c ≈ 19 Å

2 LnSF + LnOF

$Ln_3OF_3S_2$

Orthorhombic Pnnm

a ≈ 5.6 Å, c ≈ 19 Å

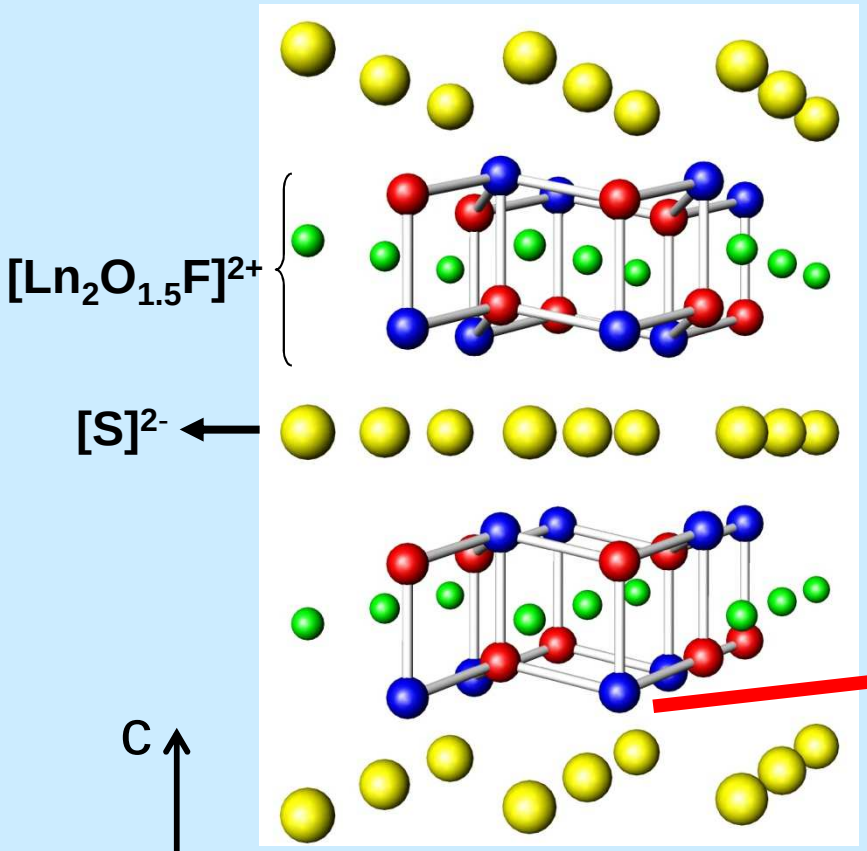

A. Demourgues et al. , J. Alloys Comp, 2001, 323, 223-230

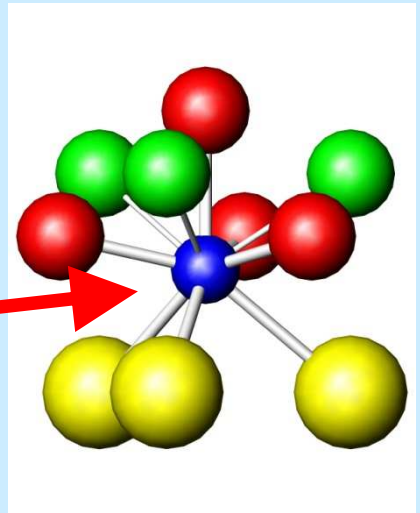
D. Pauwels, A. Demourgues et al .Solid State Sciences, 2002, 4,. 1471-1479.

# *A new class of compounds : rare earth oxyfluorosulfides*

**Modification of the charge (ionicity) of '[Ln-O,F]' blocks : single sulphur sheet**

**Powder X-ray and Neutron Diffraction analysis**



$Ln_2O_{1.5}FS$

Hexagonal P-3m1

a ≈ 4.1 Å, c ≈ 6.9 Å

D. Pauwels, A. Demourgues et al .Solid State Sciences, 2002, 4,. 1471-1479.

## *A new class of compounds : rare earth oxyfluorosulfides*

**Double sulphur sheets : $LaFS = [La_2F_2]^{4+} + [S_2]^{4-}$**

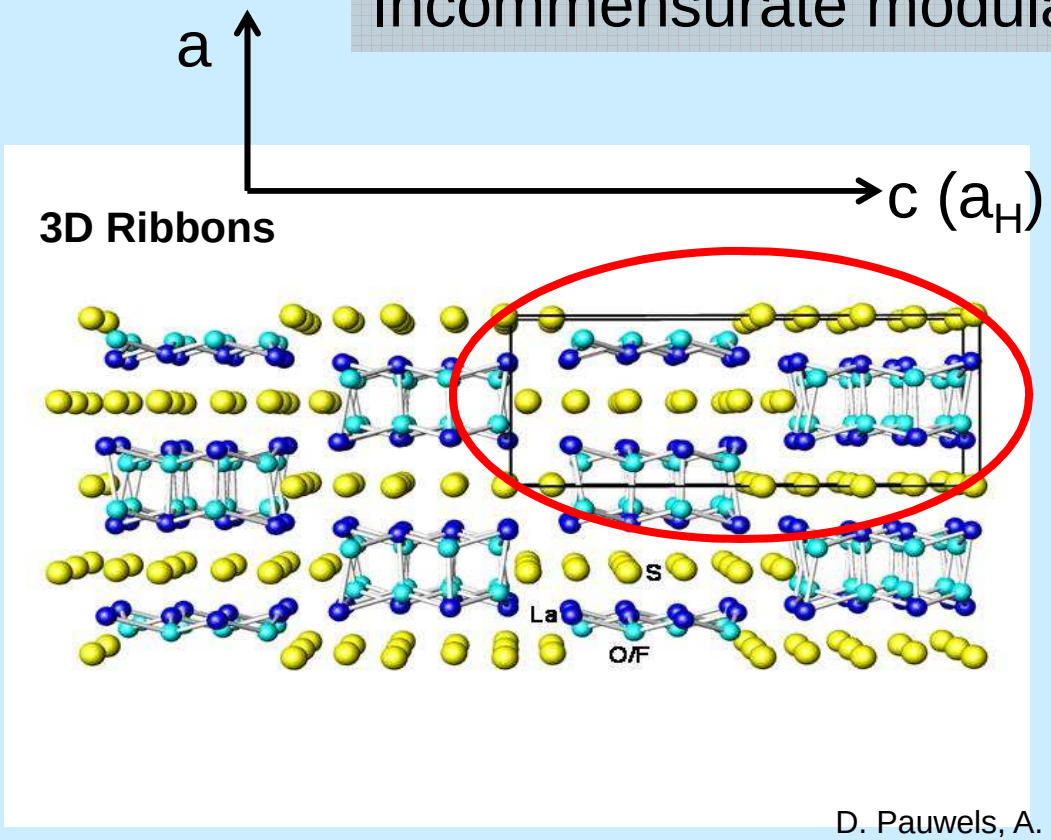
**Double sulphur sheets : $La_3OF_3S_2 = [La_3OF_3]^{4+} + [S_2]^{4-}$**

**Single sulphur sheets : $La_2O_{1.5}FS = [La_2O_{1.5}F]^{2+} + [S]^{2-}$**

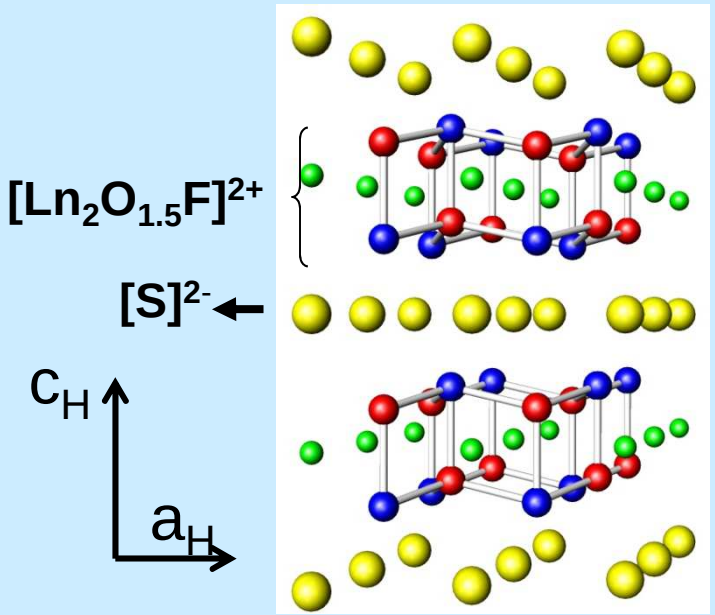
Occurrence of '[Ln-O,F]' blocks with 3+ charge ??

# $La_4O_2F_2S_3 = 2\,[La_2OF]^{3+} + [S_2]^{4-} + [S]^{2-}$ ??

Incommensurate modulated structure




$La_2O_{1.5}FS = La_2O_2S$

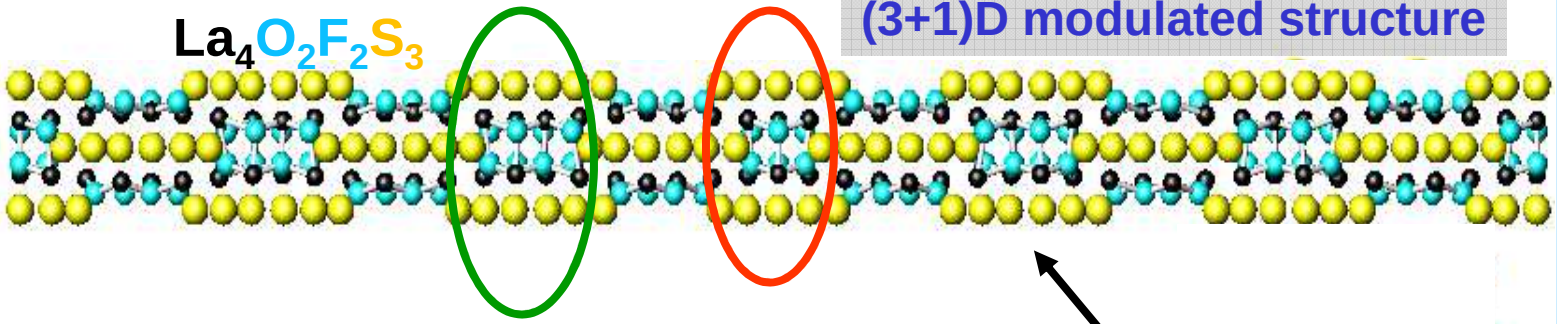



D. Pauwels, A. Demourgues et al. Chem Mater. 2006, 18, 6121-6131

# *A new class of compounds : rare earth oxyfluorosulfides*

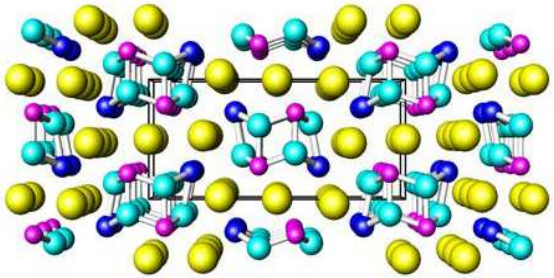
$La_4O_2F_2S_3$

(3+1)D modulated structure

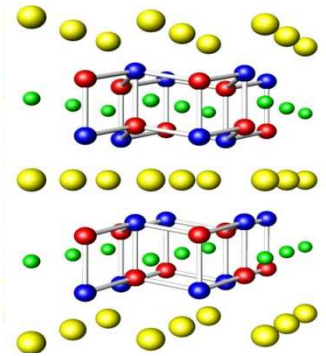


$(Ce^{3+},Ce^{4+})O_4S_3 = (La,Y)_4O_2F_2S_3$

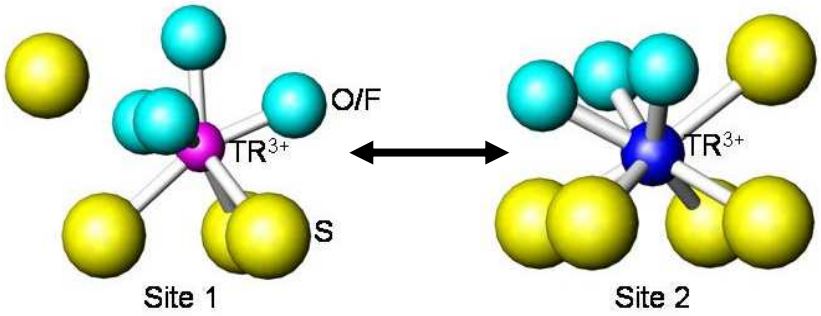
3D structure
Pbam



Shear plane mechanism



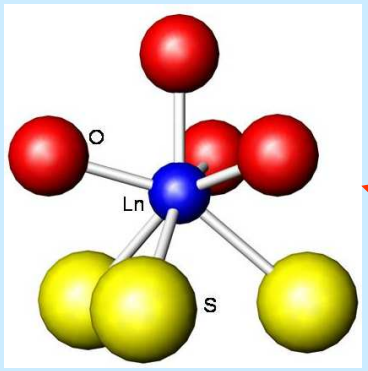
$La_2O_{1.5}FS = La_2O_2S$




***For $La_4O_2F_2S_3$ various site geometries between site 1($Y^{3+}$) and site 2 ($La^{3+}$)***

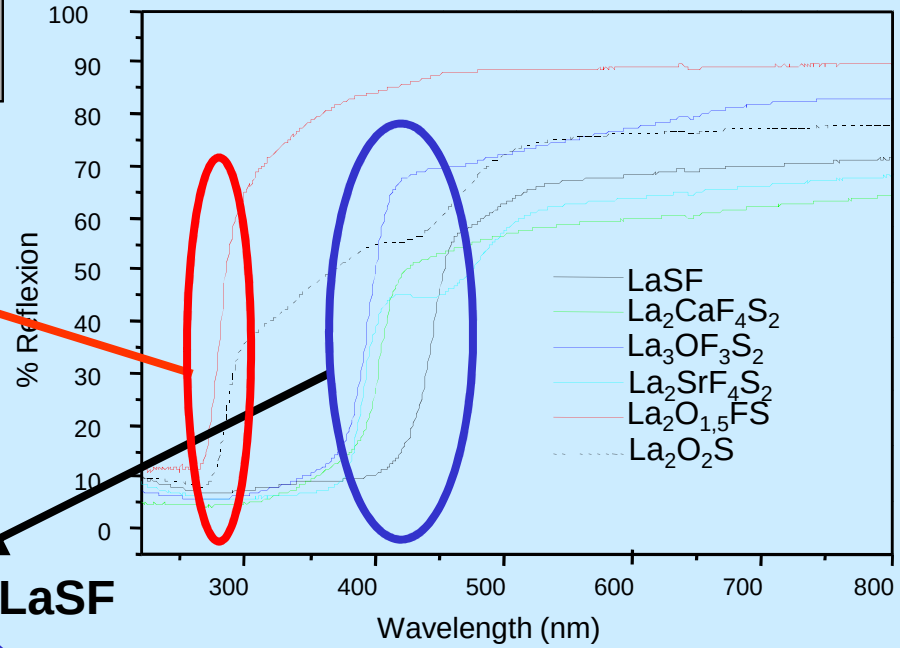
***Competition between Fluorite-type blocks ('ionic' ) and Sulphur sheets ('covalent') : Key role of the charge/size of Fluorite block (O/F) and the nature of rare earth***

# *Rare earth oxyfluorosulfides and optical absorption properties*

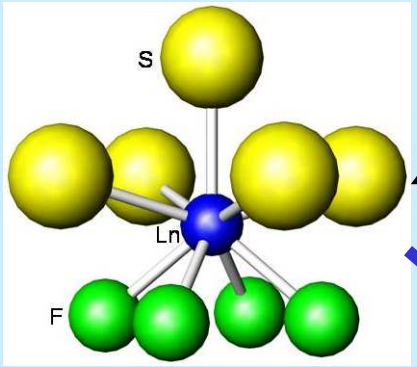



**d(La-O) ≈ 2.45 Å × 4**
**d(La-S) ≈ 3 Å × 3**

$La_2O_2S = La_2O_{1.5}FS$

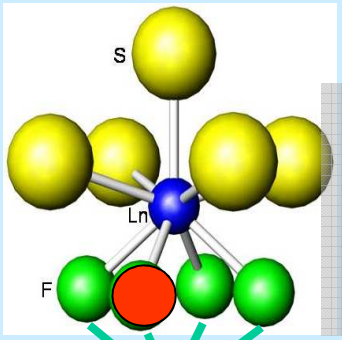



**d(La-O) ≈ 2.5 Å × 4**
**d(La-S) ≈ 3 Å × 5**




**LaSF**

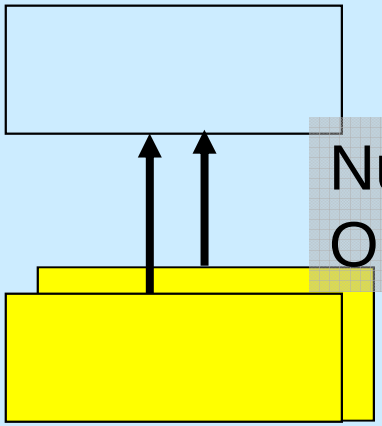
**$La_3OF_3S_2$**
**$La_2AF_4S_2$**




**Relaxation of Sulphur sheets**
**S-S distances ↑**
**Optical band gap ↑**

**A, Ln**

**[La(A)-F,O] blocks A/Ln-F/O bond distances ↓**

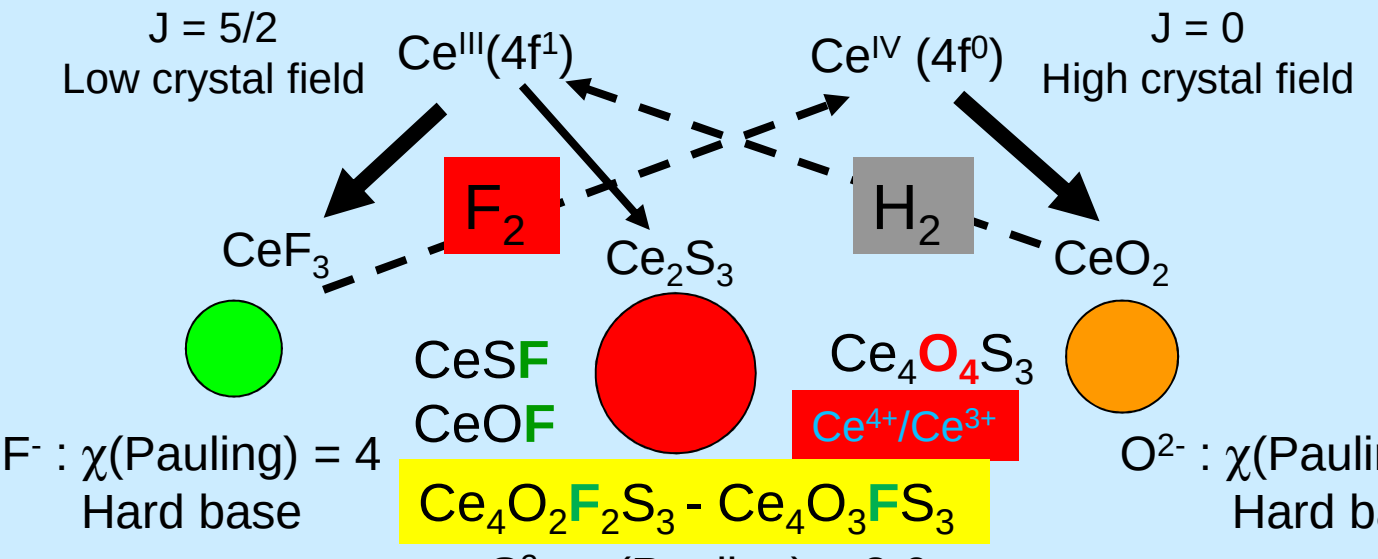


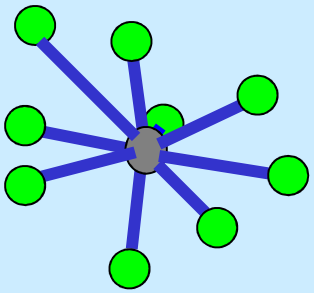
4f,5d(La)

Number of S atoms ↑
Optical band gap ↓

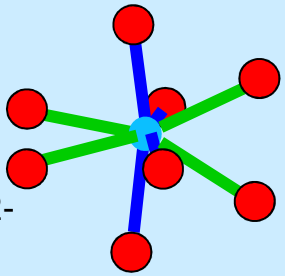
3p(S)

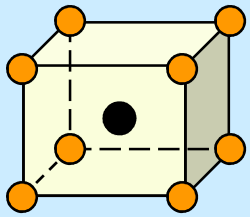
# *The Ce valence states in fluorides, oxides and sulfides*



Low crystal field
Low Madelung
Potential $V_{F-}$, $V_{S2-}$





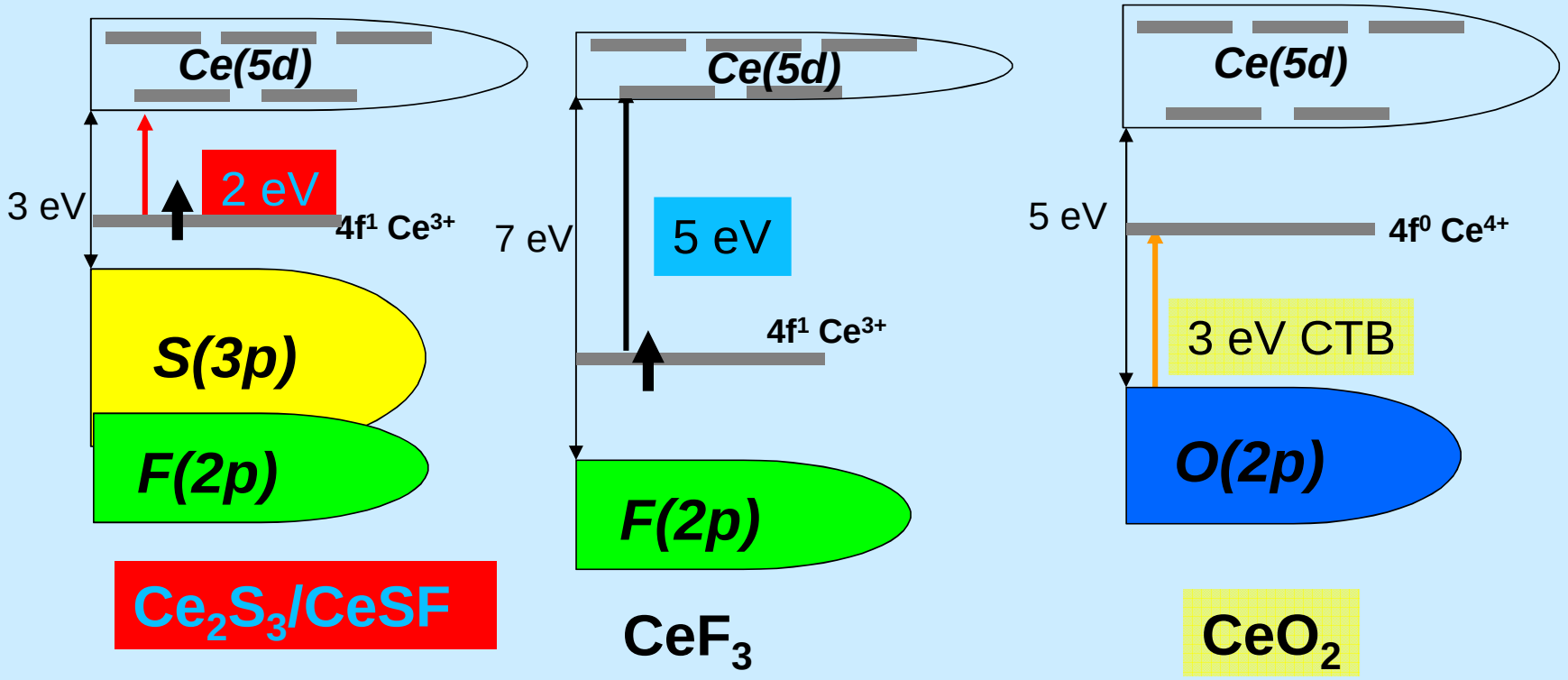
High crystal field
High Madelung
Potential $V_{O2-}$

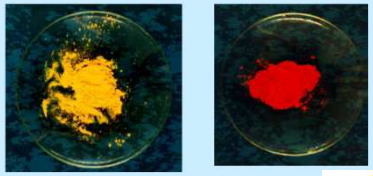
Distorted
Polyhedron [9]
Ce-F = 2.40-2.53 A

Two tetrahedra
surrounding Ce [8]
Ce-S = 2.80-3.00 A

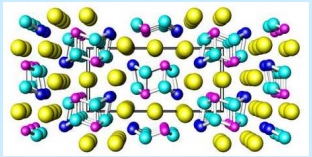
Cubic site [8]
Ce-O = 2.34 A

***From the composition and structural features of Ce compounds to the optical absorption properties***







$Ce_4O_4S_3$: Semiconducting behavior (4f)

$Ce^{4+}/Ce^{3+}$ $Ce_4O_{4-x}F_xS_3$ **(p-type SC ?)**

# *Structural relationships with RE $T_M P_N O_{1-x}F_x$ oxypnictides*

- **LaFS** = PbFCl = BiOCl
- Charge density into Layers $(LaO)^+$ -Fluorite- and $(FeAs)^-$ -Anti Fluorite-

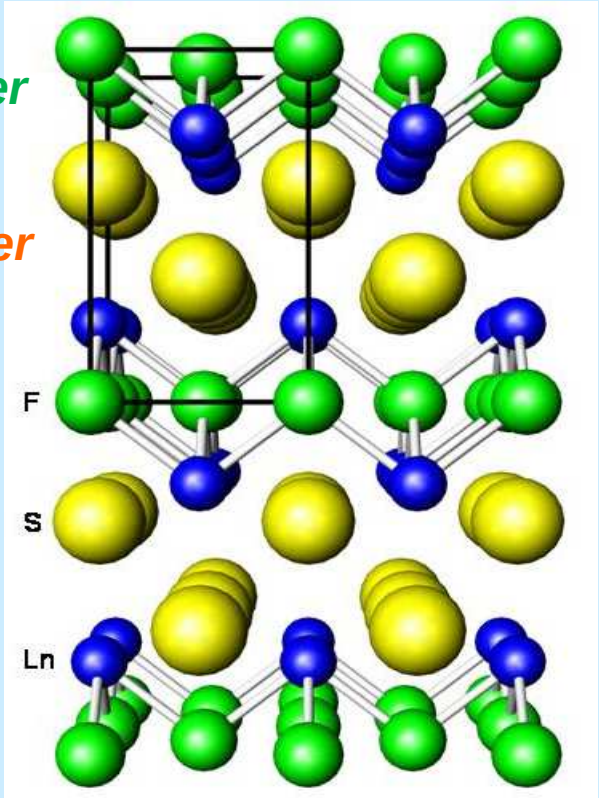
→ ***e- Transfer : $LaO_{1-x}F_xFeAs$***

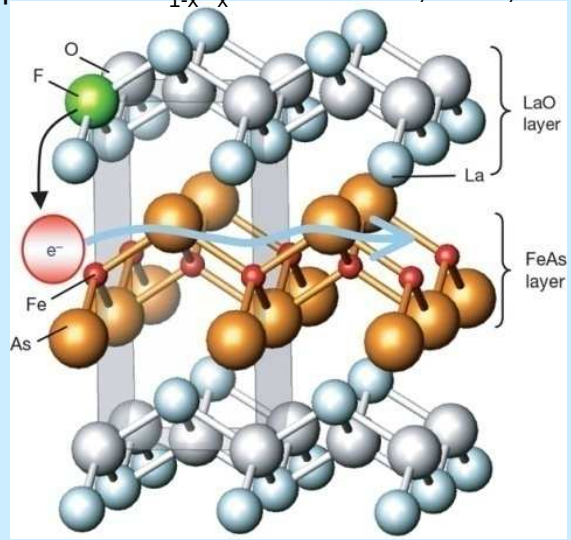
– LaO « réservoir » layer ⟹ FeAs conducting layer

Takahashi, H. et al. Superconductivity at 43K in iron-based layered compound .$LaO_{1-x}F_x$FeAs. *Nature*, 2008, **453**, 376-378

***$(LaF)^{2+}$ layer***

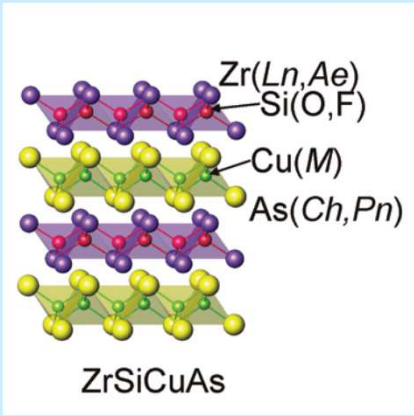
***$(S)^{2-}$ layer***



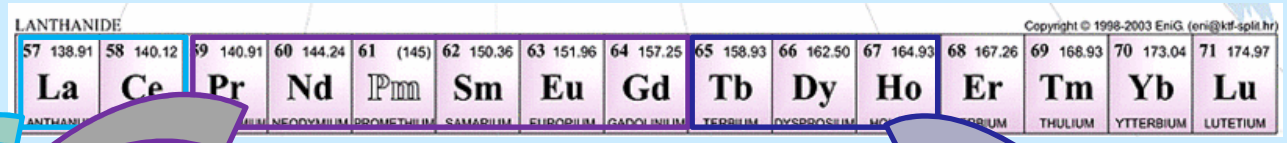

***$(LaO)^+$ layer***

***$(FeAs)^-$ layer***



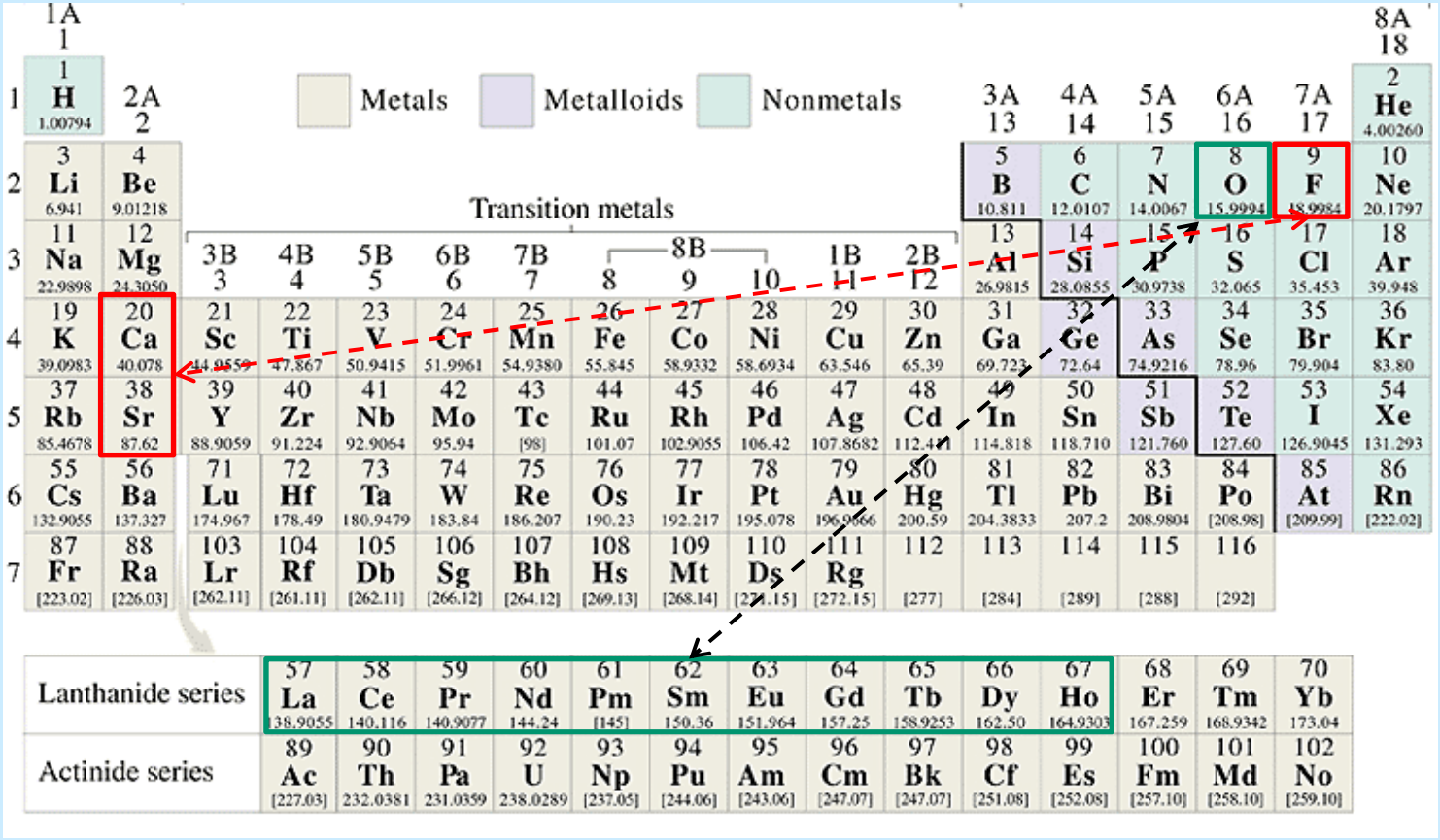

: B.I. Zimmer , W. Jeitschko et al. J. Alloys and Comp, 1995, **229,** 238

# Superconducting Fe-As Materials : influence of Rare Earth series



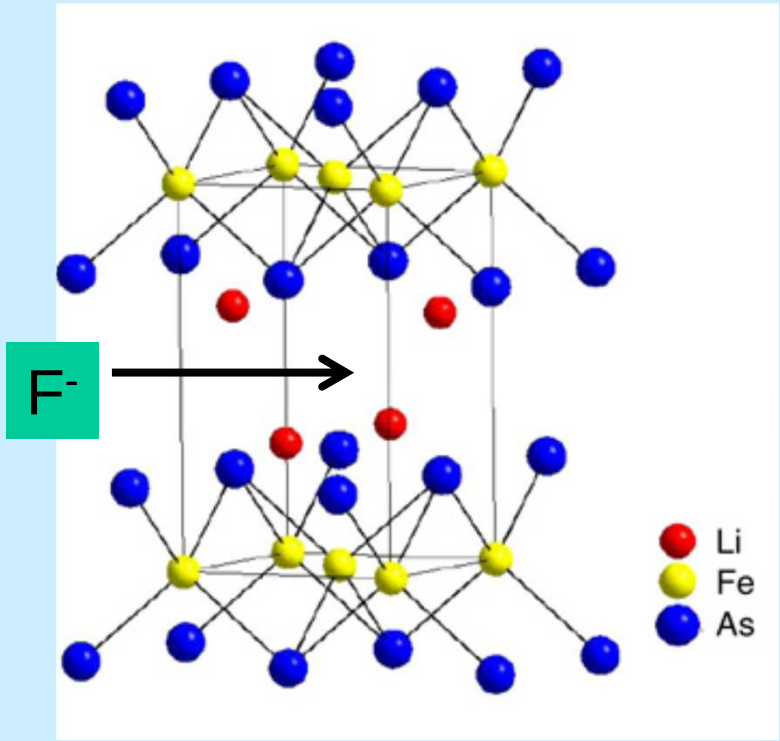

| Formule chimique | $T_c$ |
|---|---|
| $LaFeAsO_{0,85}F_{0,15}$ , $LaFeAsO_{0,85}$ | 26 K, 43 K à 4 GPa |
| $LaFeAsO_{0,6}F_{0,4}$ | 41K (synthèse HP à 6GPa) |
| $La_{0,88}Sr_{0,12}FeAsO$ | 25 K , dopage trous |
| $CeFeAsO_{0,8}F_{0,2}$ | 41 K |
| $PrFeAsO_{0,85}F_{0,15}$ , $NdFeAsO_{0,6}F_{0,4}$ | 50-52 K |
| $SmFeAsO_{0,85}$, $SmFeAsO_{0,9}F_{0,1}$ | **55 K** |
| $SmFeAsO_{0,85}F_{0,15}$ | 43 K |
| $GdFeAsO_{0,85}$, $GdFeAsO_{0,8}F_{0,2}$ | 53,5-51,2 K |
| $HoFeAsO_{0,8}$ | 50,3 K |
| $YFeAsO_{0,8}$ | 46,5 K |
| $DyFeAsO_{0,8}$ | 52,2 K |
| $TbFeAsO_{0,8}$ | 48,5 K |

- ***AFeAsF compounds : layers $(A^{2+},F^{-})^{+}$***




| Compounds | $T_c$ |
|---|---|
| $CaFe_{1-x}Co_x AsF$ | 22 K |
| $Sr_{0,8}La_{0,2}FeAsF$ | 36 K |
| $Sr_{0,5}Sm_{0,5}FeAsF$ | 56 K |

- $Li_{1-x}FeAs$ compounds
  - $Li^+ (FeAs)^-$, $T_c = 18$ K
  - Structural features :
    - FeAs layers
    - Inserted $Li^+$




**LiFeAs(F) : $V_M(F^-) = -3.5$ V !**
**NaFeAs(F) : $V_M(F^-) = -1.08$ V !**

**$V_M (As^{3-}) =$ + 28 V / + 31 V**

Wang, X.C. et al. 2008. The superconductivity at 18K in LiFeAs system. *Solid State Communications*, **148**, 538-540.

## *Structural parameters which influence superconducting properties of $REO_{1-x}F_xFeAs$ compounds*

- Parameters which influence $T_c$ :
  - Doping with $F^-$
    - ***Increasing of electron density*** into FeAs layers
  - Application of High Pressure

Reduction of cell parameters

- 2D Structure and critical temperature $T_c$ :
  - ***Converging to*** Tetrahedron $FeAs_4$ **[Td]** ***Symmetry***
  - ***Inter layers*** $Fe_2As_2$ ***distance increasing***

| Compounds | $T_c$ |
|---|---|
| $CaFe_{1-x}Co_x AsF$ | 22 K |
| $Sr_{0,8}La_{0,2}FeAsF$ | 36 K |
| $Sr_{0,5}Sm_{0,5}FeAsF$ | 56 K |

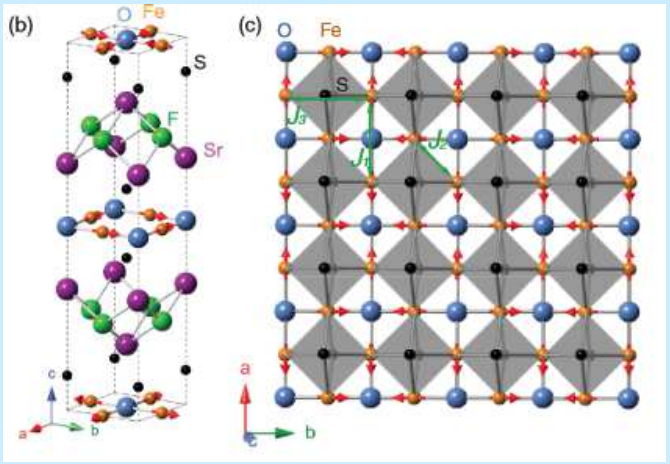
# The $Fe^{2+}$ ($3d^6$) case stabilized in mixed anions environment

## $Sr_2F_2Fe^{2+}{}_2OS_2$ (Oh) $FeO_2S_4$ (Td) $SrF_4$

**[Fluorite blocks]**
**$[Sr_2F_2]^{2+}$**
+
[ Anti $CuO_2$ layers]
**$[Fe_2O\ (S_2)\ ]^{2-}$**

[Td] : $FSr_4$ [Td] : $OFe_4$
[Td] : $SFe_4$

Electrostatic valence (Pauling) :
2F(-2) + O (-1.33) +
2 S (-1.33) = - 8




H. Kabbour, L. Cario et al. J.A.C.S, 2008, **130**, 8261

I4/mmm
SC + 2D Ising AFM ($T_N$<110K)
S=2 AFM checkerboard spin lattice

[Rocksalt blocks]
**[6] $CaO_3S_3$**
+
**[Wutzite sheets]**
**[4] $Fe^{2+}OS_3$**

[Td] : $OFeCa_3$
[Oh] : $SFe_3Ca_3$

Electrostatic valence (Pauling) :
O (-1.5) + S (-2.5) = -4

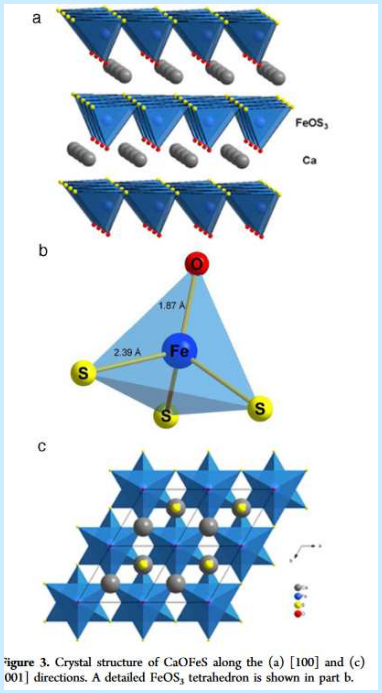



Figure 3. Crystal structure of CaOFeS along the (a) [100] and (c) 001] directions. A detailed $FeOS_3$ tetrahedron is shown in part b.

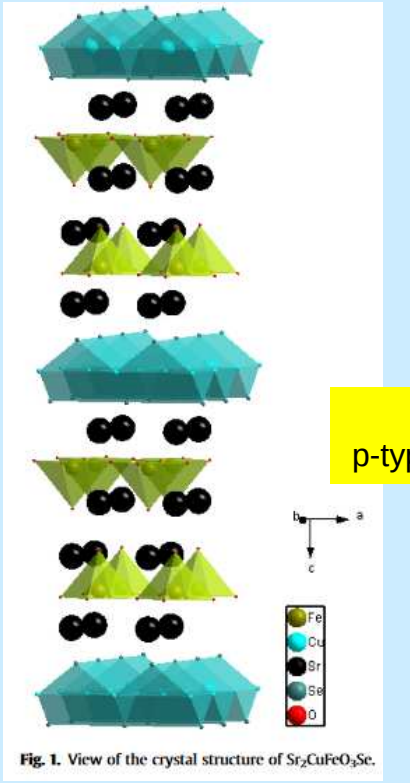



Fig. 1. View of the crystal structure of $Sr_2CuFeO_3Se$.

## $Sr_2FeCu_{0.9}O_3Se$

**$[Sr_2Ga^{3+}Cu^{+}O_3S]$**

[Perovskite layers]
**[5] $FeO_5$** [9] **$SrO_9$**
+ [4] **$SrO_4$**
**[AntiFluorite sheets]**
**[4] $CuSe_4$**

P4/nmm
p-type (Cu+)-SC + AFM ($T_N$>300K)

D. Berthebaud et al.
Sol. Stat. Sci. 2014, **36**, 94-100

***$Fe^{2+}/Cu^{2+}$*** or
***$Fe^{3+}/Cu^{+}$*** ?

[Td] : $SeCu_4$

[Oh] x 2: $OFe_2Sr_4$ , [Oh] : $OFeSr_5$

## $CaOFe^{2+}S$

(Td) $FeOS_3$

Polar structure ($P6_3mc$),
Magnetodielectric $T_N$=35K

C. Dellacotte et al. Inorg. Chem.
2015, **54**, 6560-6565

Electrostatic valence (Pauling) :
Se(-2) + 2O (-2.24) +
O (-1.51) = - 8

Electrostatic valence (Pauling) :
Se(-1) + 2O (-2.64) +
O (-1.71) = - 8

# Stabilization of various anions around Fe !
# To tune the redox/electronic/magnetic properties…

**Thin Films and electronic/magnetic properties**

**'$Fe^{2+}_{0.3}Fe^{3+}_{0.7}O_{0.35}N_{0.65}$'**

M. Grafouté, J.M. Grenèche et al.
J. Phys: Condens. Matter 19 (2007) 226207

**$^{7}N$**
Pauling : 3.0
[He] $2s^2 2p^3$

**$^{8}O$**
Pauling : 3.5
[He] $2s^2 2p^4$

**Na Battery**
**$NaFe^{2+}OF$**
**$Fe^{3+}OF$**

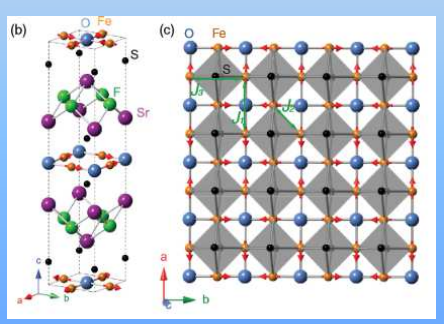
J. Zhu and D. Deng
Angew. Chem,
54 (2015), 3079

**$^{9}F$**
Pauling : 4.0
[He] $2s^2 2p^5$

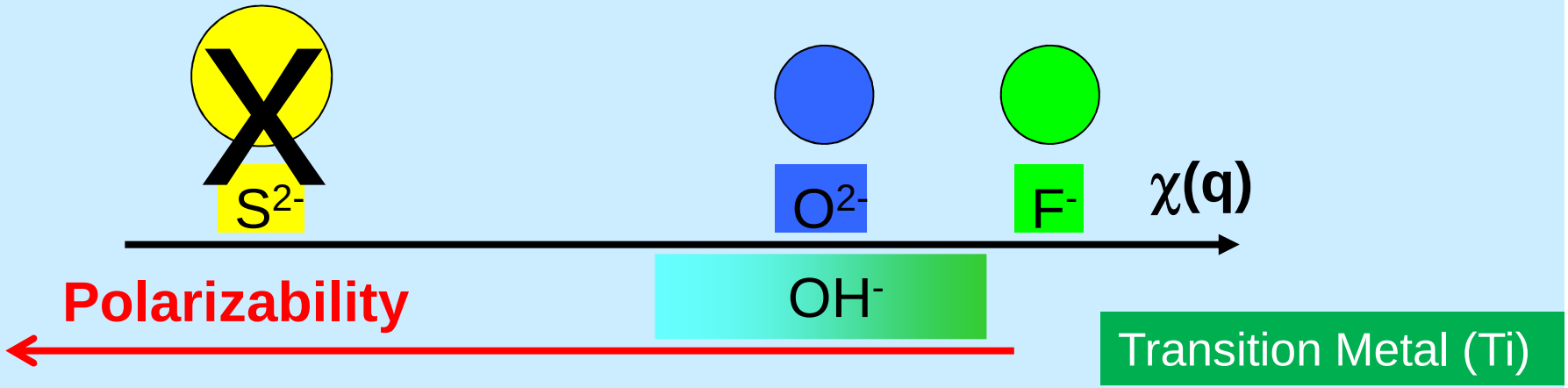
**$^{26}Fe$**
Pauling : 1.8
[Ar] $4s^2 3d^6$

**2D electronic/magnetic properties**
**$Sr_2F_2Fe^{2+}_2OS_2$**

**$^{16}S$**
Pauling : 2.6
[Ne] $3s^2 3p^4$



H. Kabbour, L. Cario et al.
J.A.C.S, 130 (2008) 8261


X
S2-
O2-
F-
χ(q)
OH-
Polarizability
Transition Metal (Ti)

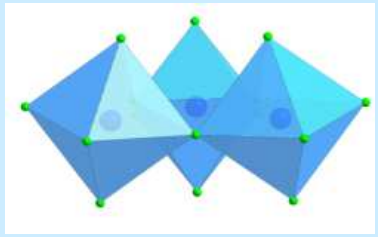
**Hydro(Solvo)thermal routes to get Ti-based mixed anions compounds**
**Influence of precursors, solvents, HF, controled T / P**

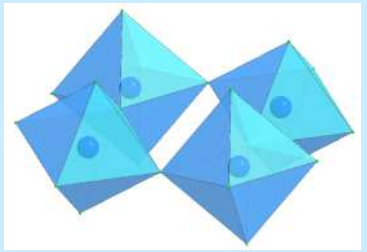
$Ti^{4+}$ : strong polarizing effect (d orbitals)

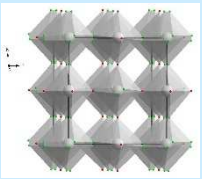
**Anionic groups X = $F^-$/$OH^-$/$O^{2-}$/ $H^-$**

**Coord Numb (X) = [1, 2, 3]**

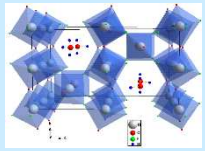
Competition



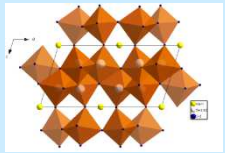


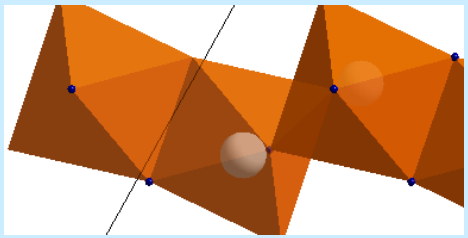


**HTB-type structure**

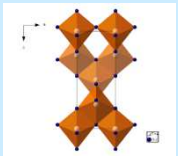


**$ReO_3$-type structure / Perovskite**





**$TiO_2$ Anatase/ (B) type-structure**

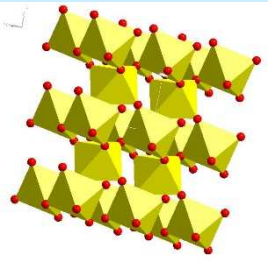


**Structural features and electronic properties**

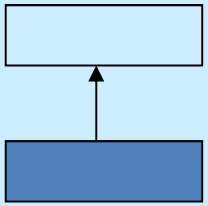

D. Dambournet, A. Demourgues et al., Chem. Mater. 20 (4), 2008, 1459–1469
D. Dambournet, A. Demourgues et al., Chem. Mater. 20 (22), 2008, 7095–7106

D. Dambournet , A. Demourgues et al., J. Mater. Chem. 18, 2008, 2483–2492

# Ti-based oxyfluorides with $ReO_3$-derived network and optical properties

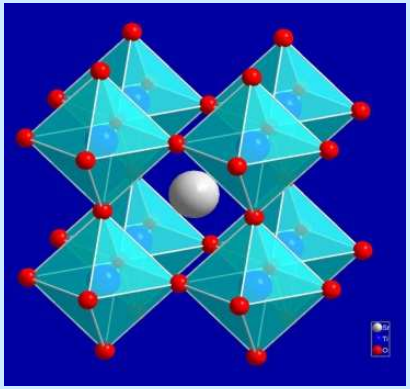


Rutile :
edge/corner
sharing octahedra
**CN(O)=3**



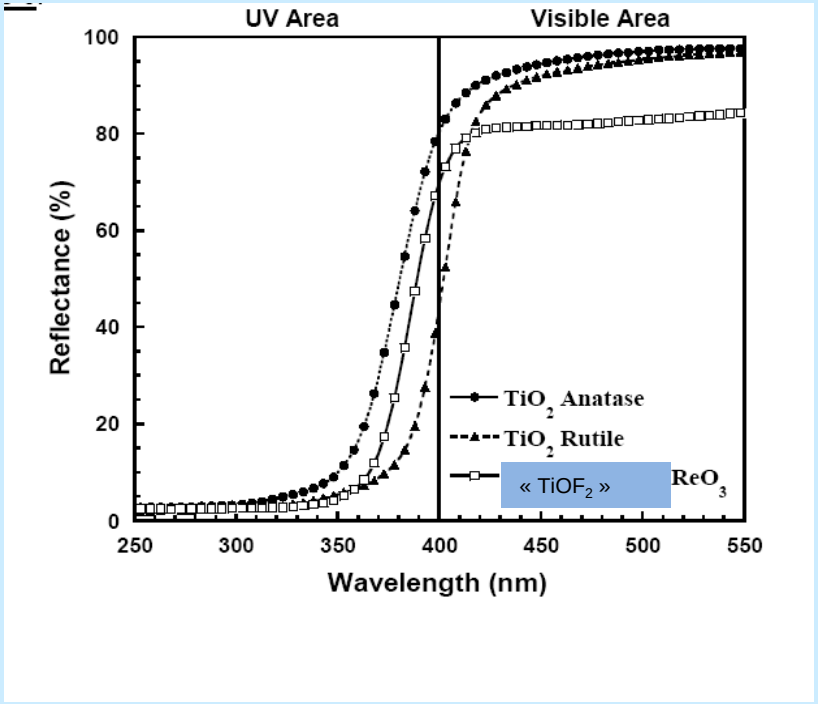

$TiO_2$ Charge Transfer Band
at 3.1-3.2 eV

$TiO_2$ + HF (anydrous or aqueous) ⟶ « $TiOF_2$ »



$ReO_3$ and Perovskite networks :
3D corner-sharing octahedra
**CN(O/F)=2**

a = 3.80 Å
(Ti-O/F = 1.90 Å)
$\rho_{exp}$ = 2.92-2.70 g.cm$^{-3}$
**$\rho_{theo}$ = 3.09 g.cm$^{-3}$**



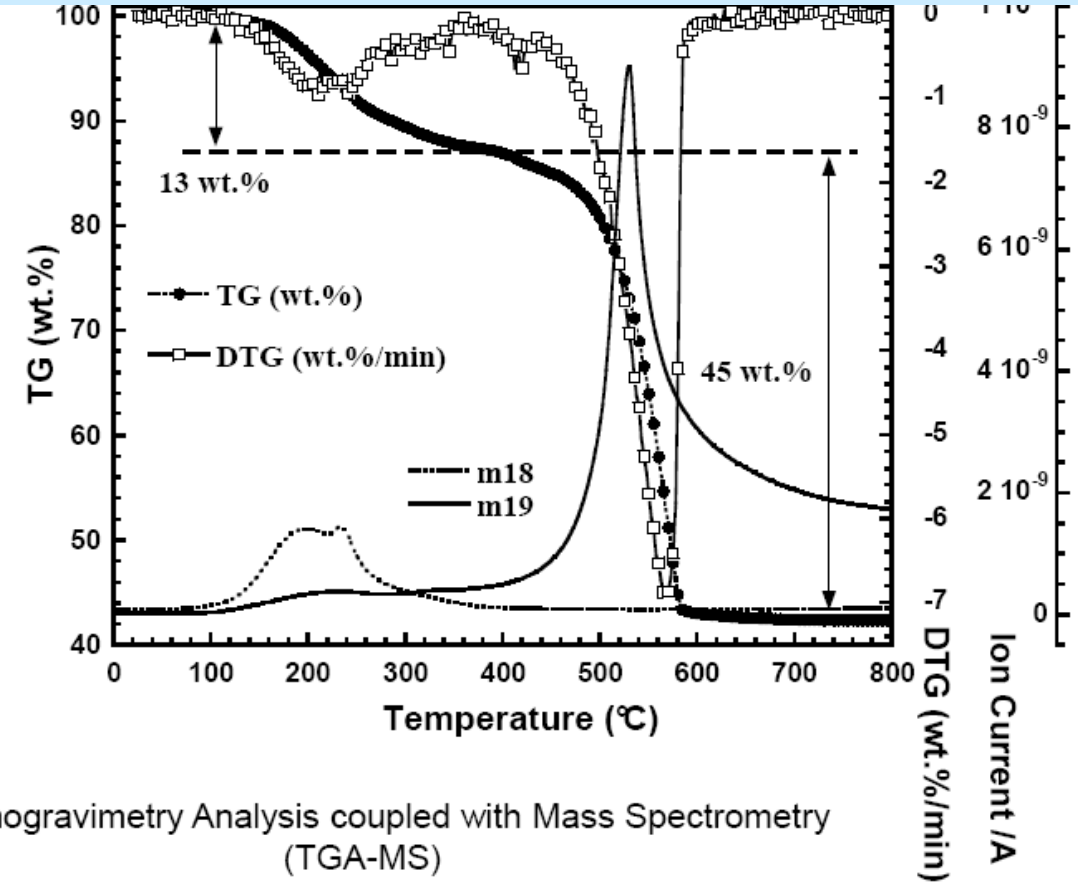

$BaTiO_3$,(Ti-O = 2.00 A) CTB : 3.4 eV

$SrTiO_3$,(Ti-O = 1.95 A) CTB : 3.6 eV

« $TiOF_2$ », (Ti-O = 1.90 A) CTB : 3.2 eV ??

# Ti-based hydroxy-fluoride with $ReO_3$-derived network

Hydrothermal route ($TiOCl_2$ , aqueous HF(40%), water as solvent, T=90°C)
R=HF/Ti=3 molar ratio



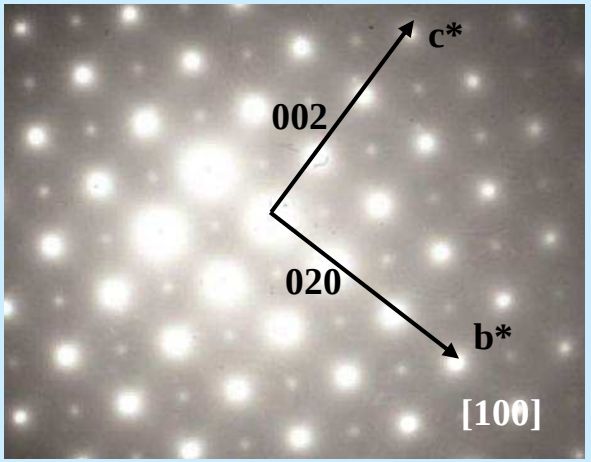

Thermogravimetry Analysis coupled with Mass Spectrometry (TGA-MS)

$OH/H_2O$ (13 wt %, T<400°C) and $TiF_4$ (45 wt%, 400°C<T<600°C) departures under $N_2$ flow

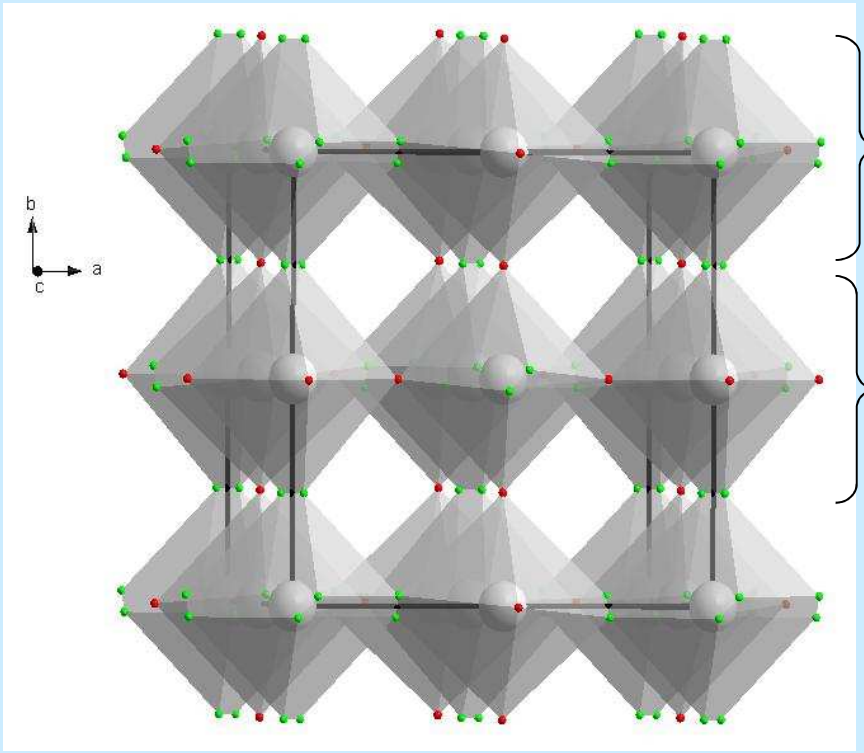
Chemical formulae : $Ti_{0.75}(OH)_{1.5}F_{1.5}$ !

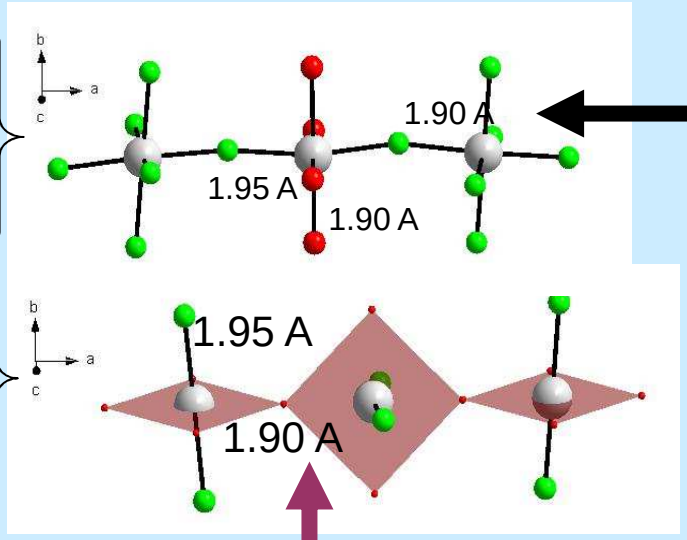
# Ti-based hydroxy-fluoride with $ReO_3$-derived network

**Electron (SG : Pn-3m)**
**X Ray, Neutron (Atomic positions)**
**diffraction investigations**




Ordered $ReO_3$ supercell
(SG : Pn-3m , a = 7.6177 A)
Ti vacancies !



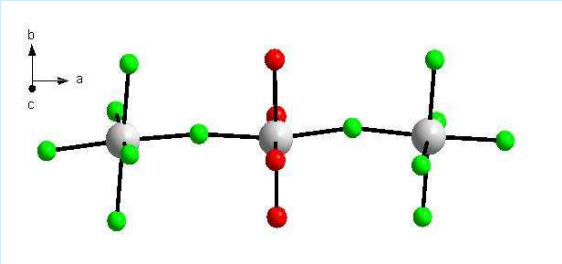

$[\ Ti_{2/3}\ \square_{1/3}\ (OH/F)_2\ F/OH\ ]_6\ [Ti\ (F/OH)_3]_2$

$\rho_{exp}$ = 2.63 g.cm$^{-3}$ ($\rho_{theo}$ = **2.70 g.cm$^{-3}$**)

A. Demourgues et al. Chem. Mater, 2009, 21, 1275-1283

# Stabilization of $Ti^{3+}$ in Titanium hydroxyfluoride : $Ti_{0.75\ \ 0.25}F_{1.5}OH_{1.5}$

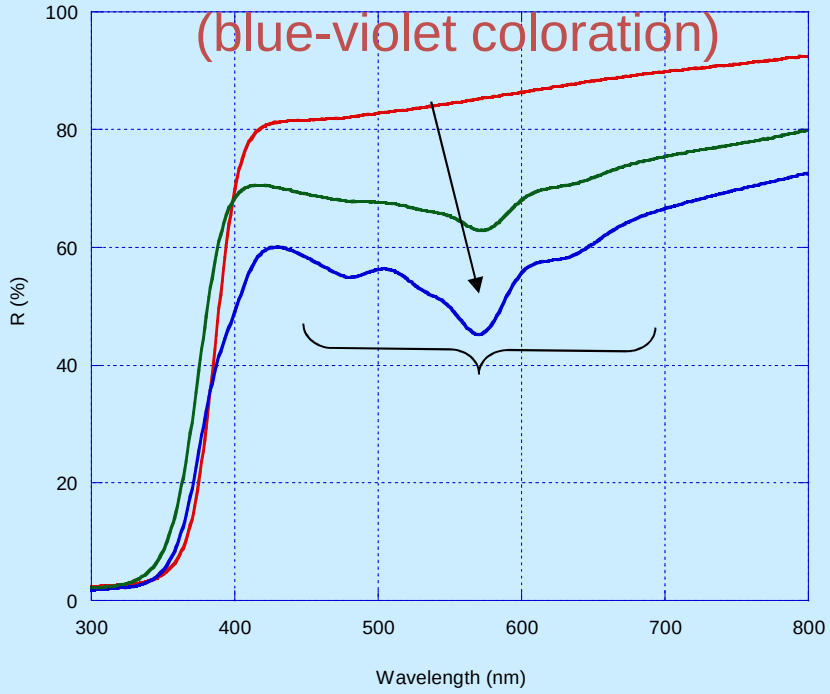
Microwave assisted solvothermal synthesis
Solvents : Water + isopropanol, Precursor : $Ti(OR)_4$ , 4(5) $HF_{aq}$ , T = 100°C
***Reductive conditions !***



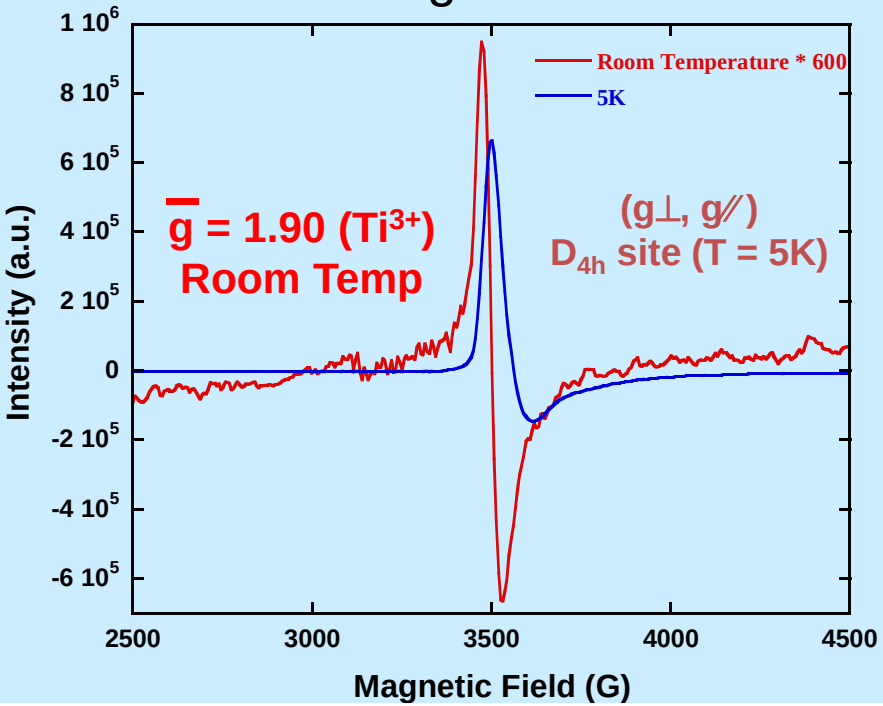

**A. Demourgues et al.**
**Chem. Mater , 2009, 21, 1275-1283**

## UV-Visible spectra

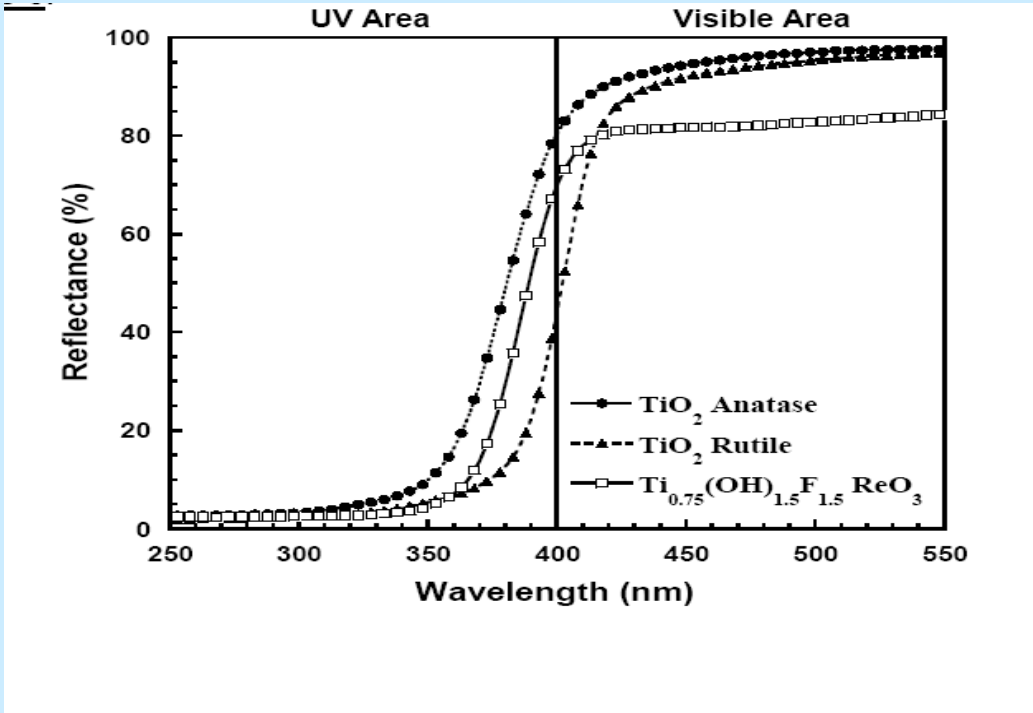
Intervalencies $Ti^{3+}$-$Ti^{4+}$
d-d transitions
(blue-violet coloration)




## ESR investigation



# Ti-based hydroxy-fluorides with $ReO_3$-derived network and band gap




**□Ti vacancies**

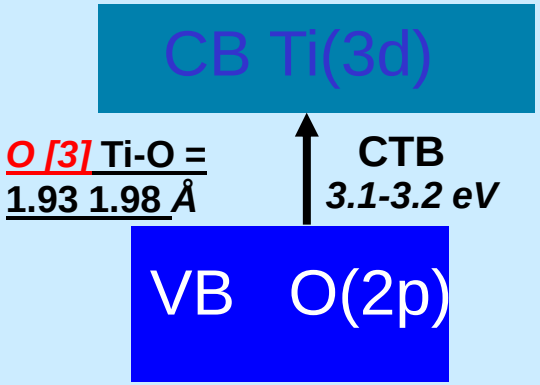
**→distorted Oh site→**

**Stabilization of CB Ti(3d)**

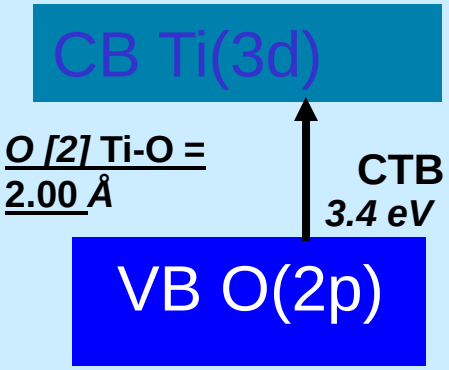
$\chi$ electronegativity

$\chi[F^-] > \chi[O^{2-}] > \chi[OH^-]$

$TiO_2$

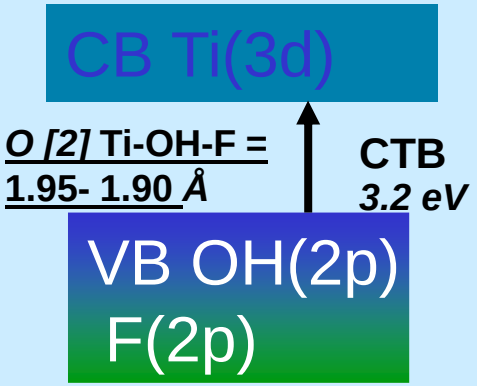



$BaTiO_3$



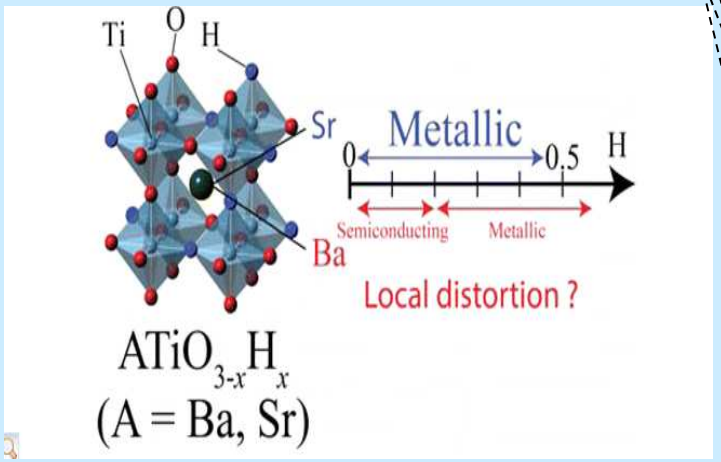

$(ReO_3)$

$Ti_{0.75}\square_{0.25}OH_{1.5}F_{1.5}$




A. Demourgues et al. Chem. Mater. 21, 2009, 1275-1283

# Ti-based Oxyhydrides with Perovskite network : $ATiO_{3-x}H_x$ (A= Ba, Sr)




G. Bouilly, H. Kageyama et al.
Chem. Mater, 2015, 27, 6354-6359

$Ti^{4+}$ ($e_g$)

$Ti^{4+}$ ($t_{2g}$)

$d_{x2-y2}$

$d_{z2}$

$d_{xy}$

$d_{xz}$

$d_{yz}$

σ* anti-bonding

π* anti-bonding

**$Ti^{3+}$**

Ti-H covalent bond

H(1s)

$O(p_\pi)$

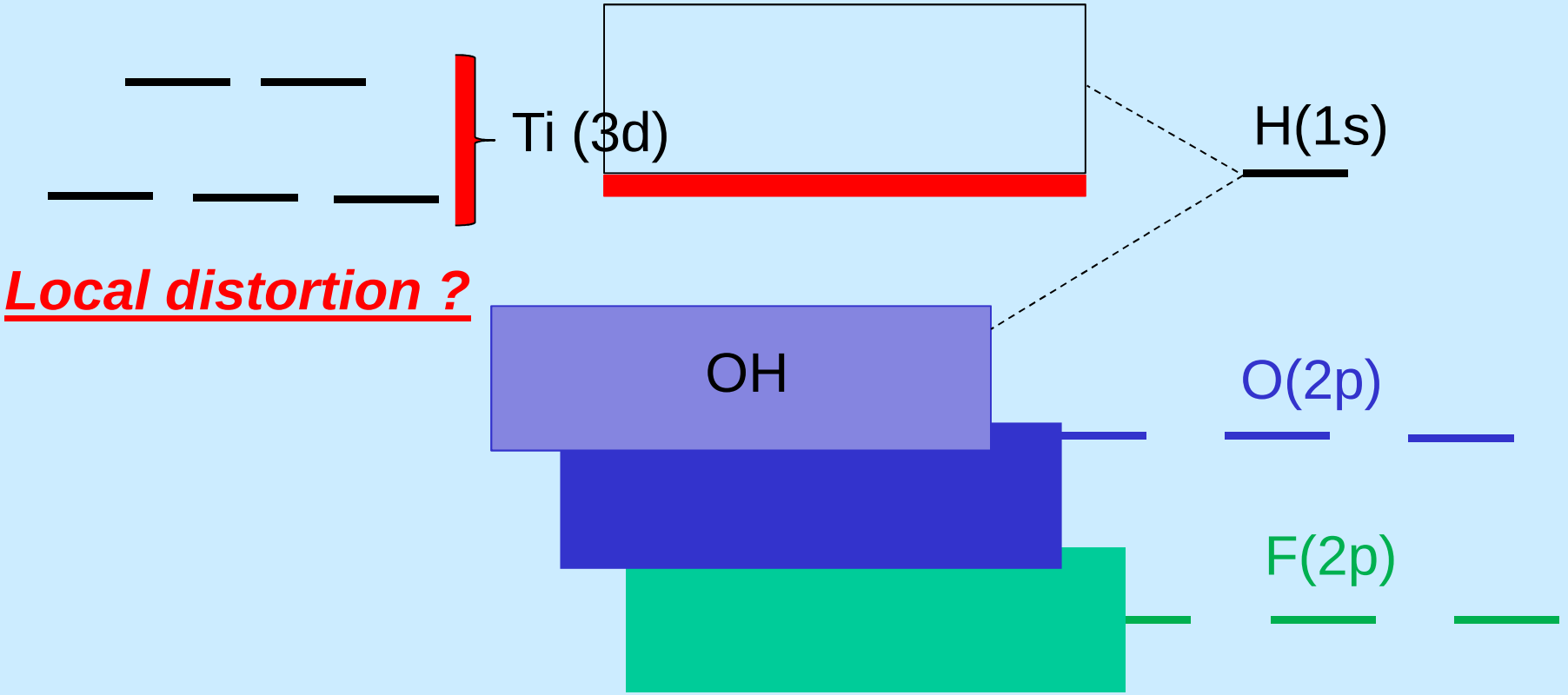
$O(p_\sigma)$

π bonding

σ bonding

Ti-H covalent bond

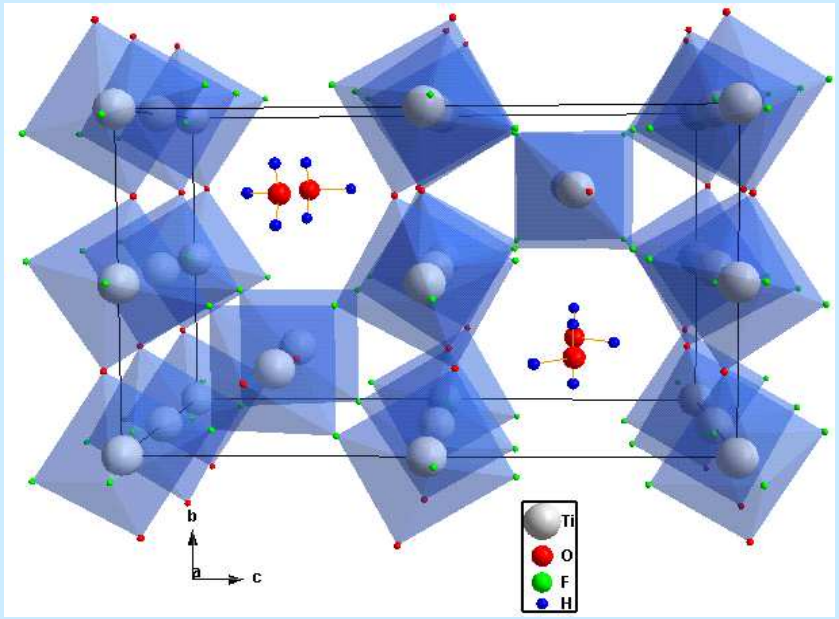
**Ti-based hydroxyfluorides and oxyhydrides :**
**How to manage the band gap ?**

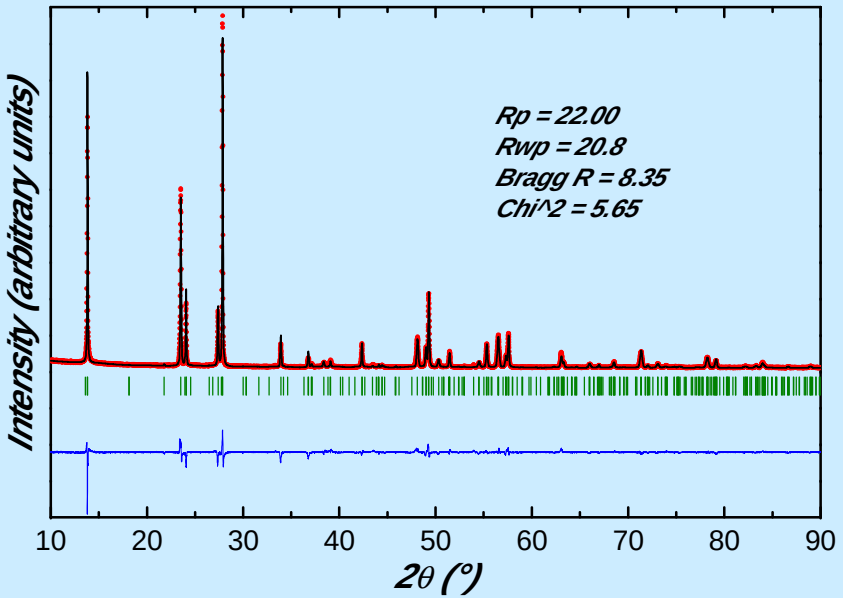



***Local distortion ?***

***Stabilization of oxy-hydroxy-fluorides ?***

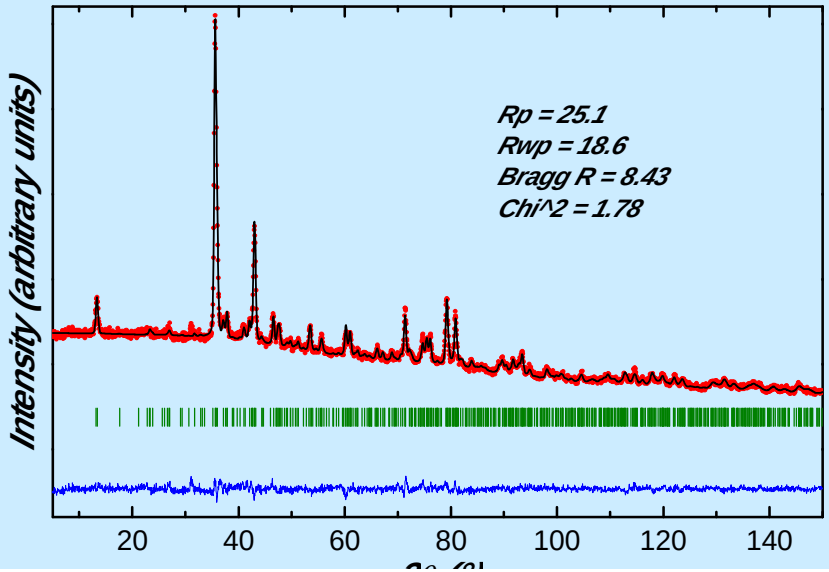
# Structural features of $Ti_{1-\varepsilon}(O,OH,F)_3$ HTB




$Ti_{0.93}O_{0.7}OH_{0.9}F_{1.4}$, 0.27 $H_2O$ (TGA/density)
Pnma, a=7.5581(1) Å, b= 7.322(1) Å, c= 12.7893(2) Å

Powder XRD Rietveld Refinement
(Cu Kα λ = 1.5406 Å)

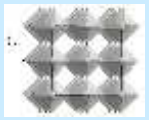



Powder Neutron Rietveld Refinement
(λ= 1.496 Å, SINQ-SWI)

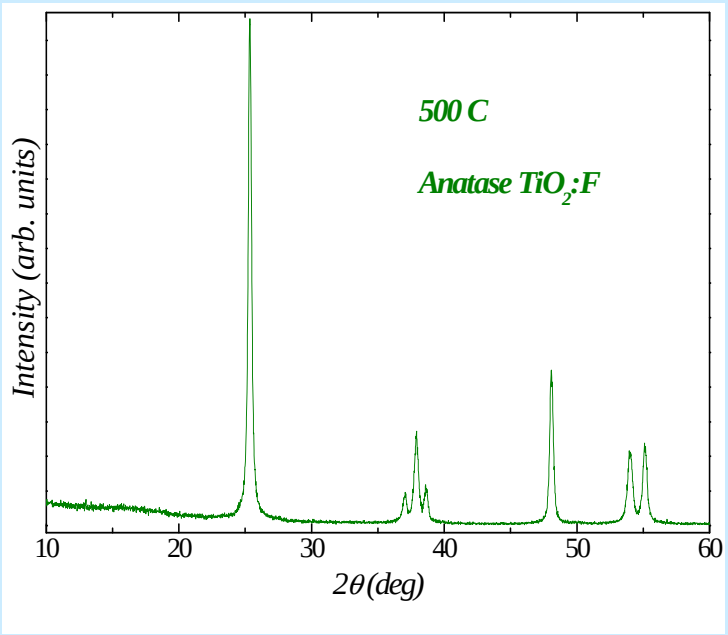
3 $TiO_2(OH,F)_4$ distorded octahedra (Neutrons) :

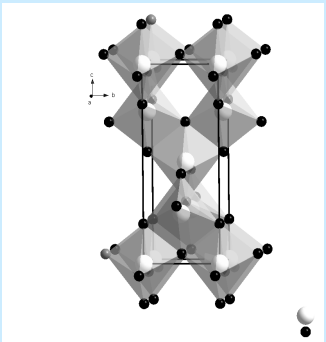
$Ti_1$ - 1.88-1.93 Å $F_1/F_2/O_2$
$Ti_2$ - 1.90-1.96 Å $F_1/O_3/F_3$
$Ti_3$ - 1.70- 2.11 Å $O_1/F_2/F_3$- Ti vacancies

# From Ti-based oxy-hydroxy-fluorides with HTB-derived network to blue conductive Anatase $TiO_2$:F

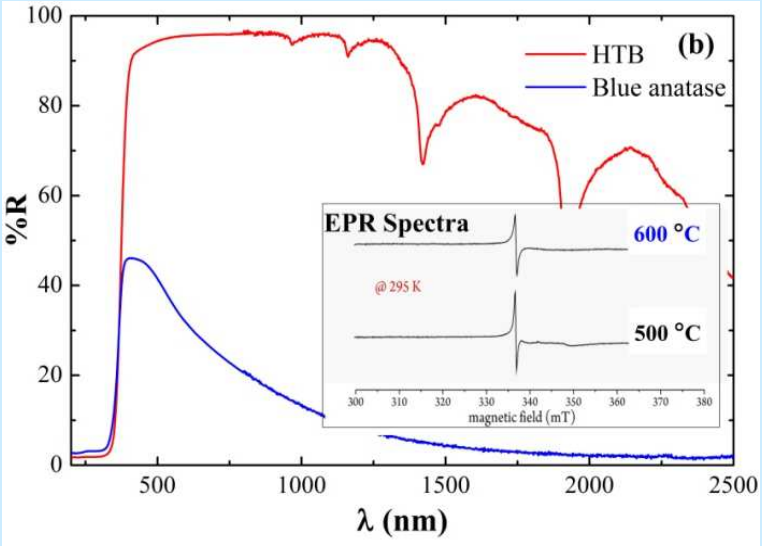


**The key role of structural/electronic defects :**
**$ReO_3$ - $Ti_{0.75}(OH)_{1.5}F_{1.5}$ → $TiO_2$ white (500°C-600°C)**
**HTB - $Ti_{0.93}O_{0.7}OH_{0.9}F_{1.4}$ → $TiO_2$: F blue (500°C-600°C)**

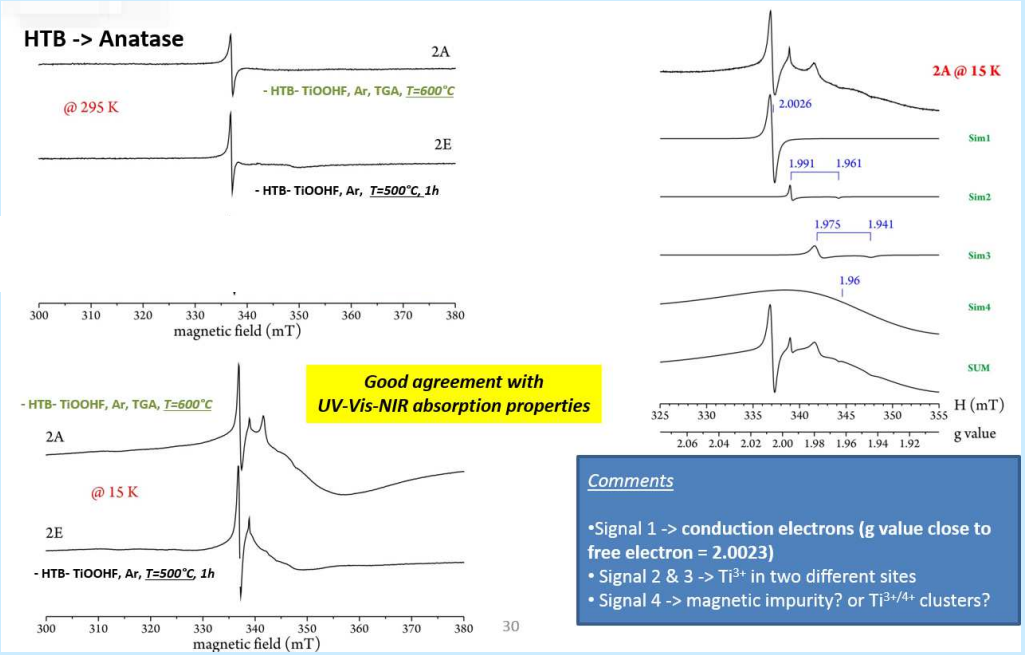


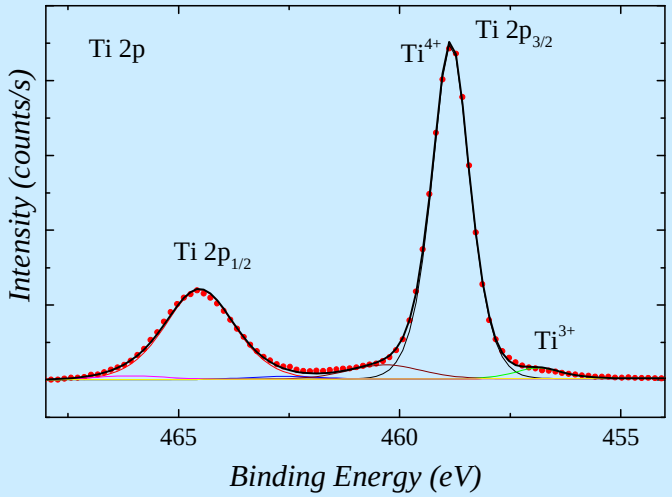
# Blue conductive Anatase $TiO_2$:F
# Strong UV and NIR absorption, conduction $e^-$ and $Ti^{3+}$.



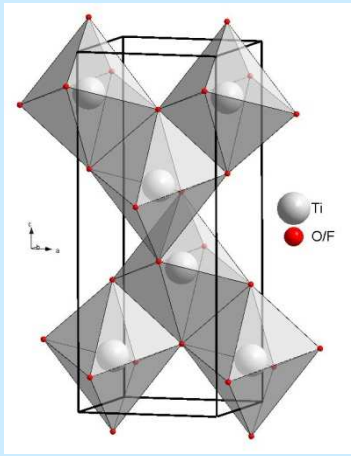

## ESR analysis

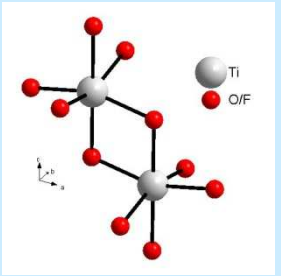



## XPS analysis



# Anatase-$TiO_2$ and orbital molecular diagram : Generation of defects induced by mixed anions compounds




**(π donors)**
***10 Dq* : $N^{3-} < F^- < O^{2-}$**

$Ti^{4+}$ ($e_g$)

$Ti^{4+}$ ($t_{2g}$)

$d_{xz}$ $d_{yz}$ $d_{xy}$

σ* anti-bonding

π* anti-bonding

$d_{xy}$ non-bonding

***Non-bonding character of $d_{xy}$ orbitals, 4 interactions $Ti^{4+}$ - $Ti^{4+}$ at 3.04 Å***

$d_{xy}$ (Ti) and $p_\pi$ (O) levels with ***non-bonding character***

p(π) N

$O(p_\pi)$

$p_\pi$ non-bonding

$O(p_\sigma)$

π bonding

σ bonding

Dense pellet obtained by SPS (82%)
(T=600°C, P=100 MPa)
$TiO_2$: Nb (2%) / F (1%)

Conductivity σ(RT) = 0.2 $\Omega^{-1}cm^{-1}$

Seebeck coefficient α(RT) = -77μV/K

**V/Z [TiNF]** = V/Z[$TiO_2$] = **17 $A^3$**

*Ti-Ti (**TiNF**)*= ***3.03 A***

**> $R_c$=3.00 A (Goodenough)**

➢ **Localized electrons**

# ***Conclusions***

*How to build mixed anions 2D network* ?

- The simple key role of electronegativity $\chi$ and polarisability $1/\eta$ of elements
- Hard-Hard and Soft-Soft Acid-Base rule
- $\Sigma n_i(M_i)v_i/Cn_i$ ($M_i$ with lower $\chi$) = $\Sigma Zi$ ($X_i$ with higher $\chi$) (extension of 2nd Pauling rule)

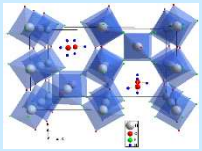
***The main networks :***

- **Ionic blocks (F/O)** vs **covalent sheets (S/Se)**
- **Fluorite, Perovskite, Rocksalt** vs **anti-Fluorite, anti-$CuO_2$, Würtzite, …**

.

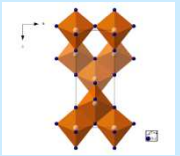
***The key role of $F^-$ : the highest $\chi$ and its anomalous properties !***

***Designing new compounds (tuning $M^{n+}$ oxidation states)***



***2D/3D Ribbons ($S^{2-}$, $O^{2-}$, $F^-$ )***

***vs 3D ($OH^-$, $O^{2-}$, $F^-$, $H^-$ ) networks / zig-zag chains***



***Tuning the band gap and opto-electronic properties by playing with competitive bonds around $M^{n+}$***

***Precursors to generate defects into oxides***