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The 1D  $A_7B_7O_{30}$  crystal lattice : an extreme case of oxygenation/slicing of 3D  $ABO_3$  perovskite



**Le Mans**  
**Université**



# The 1D $A_7B_7O_{30}$ crystal lattice : an extreme case of oxygenation/slicing of 3D $ABO_3$ perovskite

## Outline

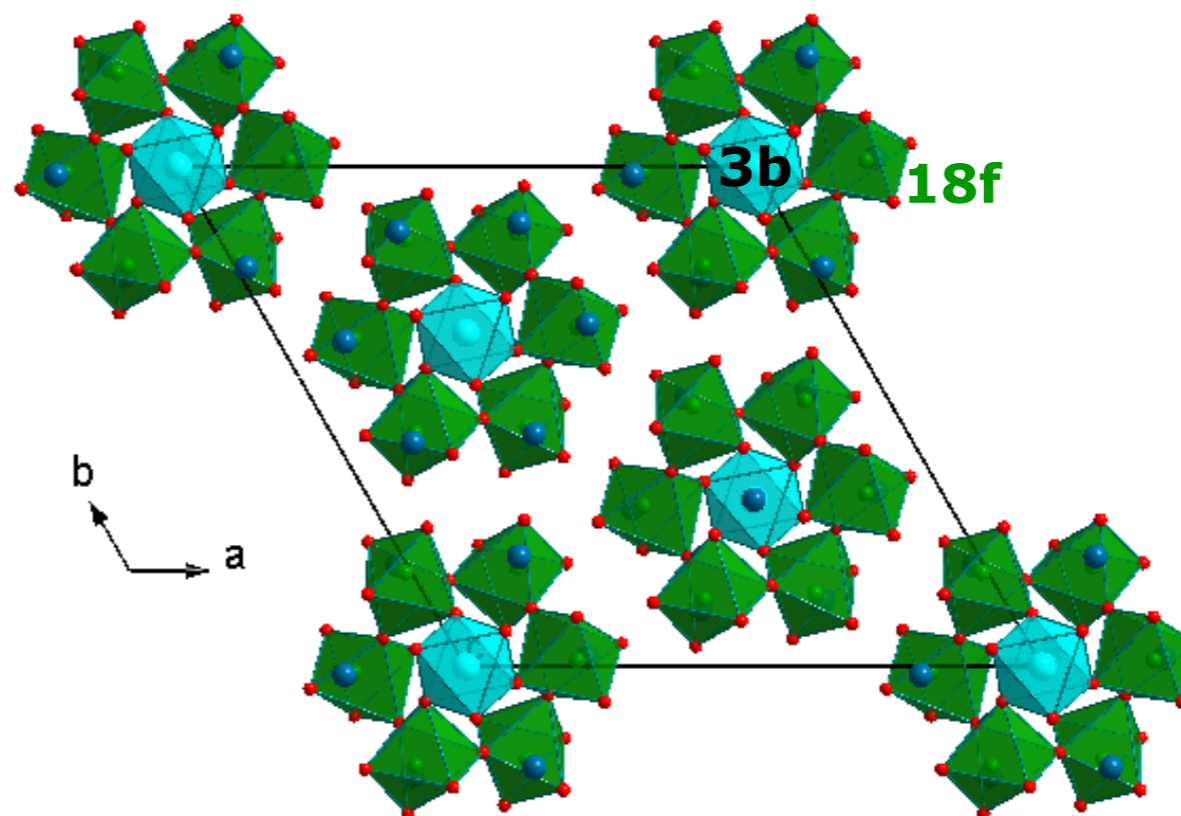
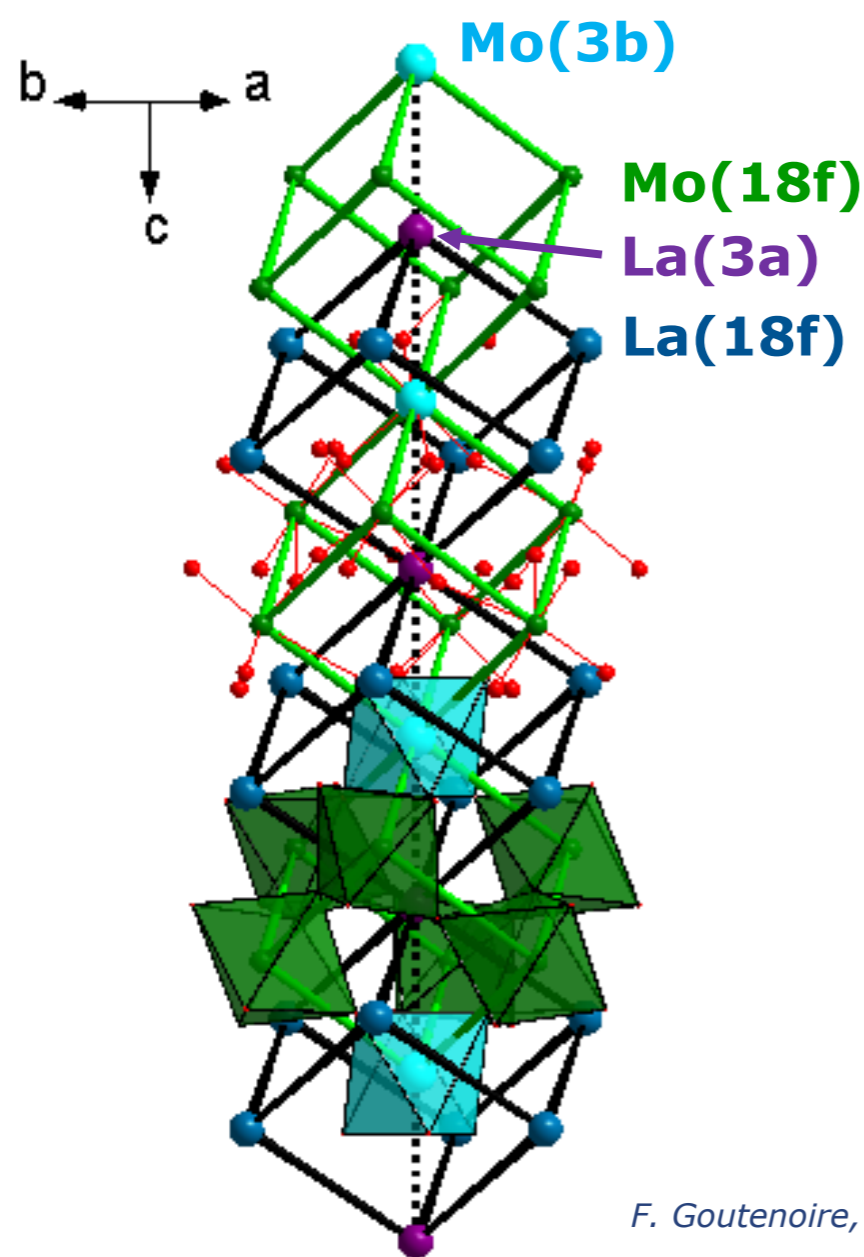
- **1) The columnar perovskite  $A_7B_7O_{30}$  crystal lattice**
  - Parent compound  $La_7Mo_7O_{30}$
  - Tungsten derivatives with transition metal substitutes
- **2) Oxygen excess in  $ABO_{3+\delta}$  type perovskites**
  - From 3D to 2D lattices:  $A_kB_kO_{3k+1}$  Dion-Jacobson and  $A_nB_nO_{3n+2}$  series
  - $A_7B_7O_{30}$  as a 1D extension of oxygenation in  $n=3$  perovskite slabs
- **3) Other members of the  $A_7B_7O_{30}$  family: the  $MPr_2W_2O_{10}$  case**

# The 1D $A_7B_7O_{30}$ crystal lattice

First evidenced in  $La_7Mo_7O_{30}$

Space group  $R\bar{3}$

- Partial reduction product of oxide-ion conductor  $La_2Mo_2O_9$
- $La_7Mo_7O_{30} \cong LaMoO_{4.286} \rightarrow Mo^{+5.57}$
- $7 Mo^{+5.57} = 1 Mo^{+4.5} (3b) + 6 Mo^{+5.75} (18f)$
- $[La_8]$  pseudo-cubes larger than  $[Mo_8]$  pseudo-cubes

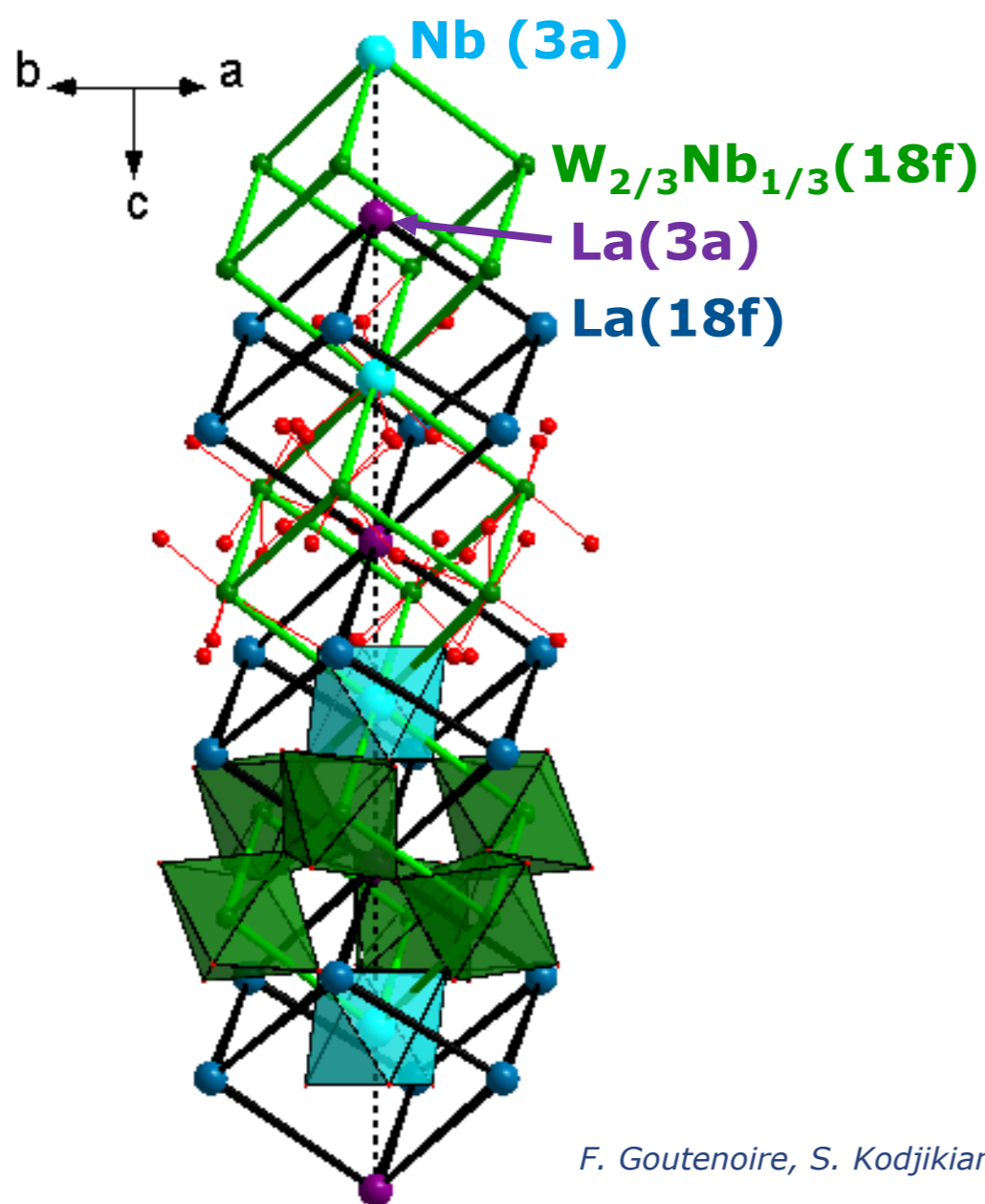


*F. Goutenoire, R. Retoux, E. Suard, P. Lacorre, J. Solid State Chem. 142 (1999) 228*

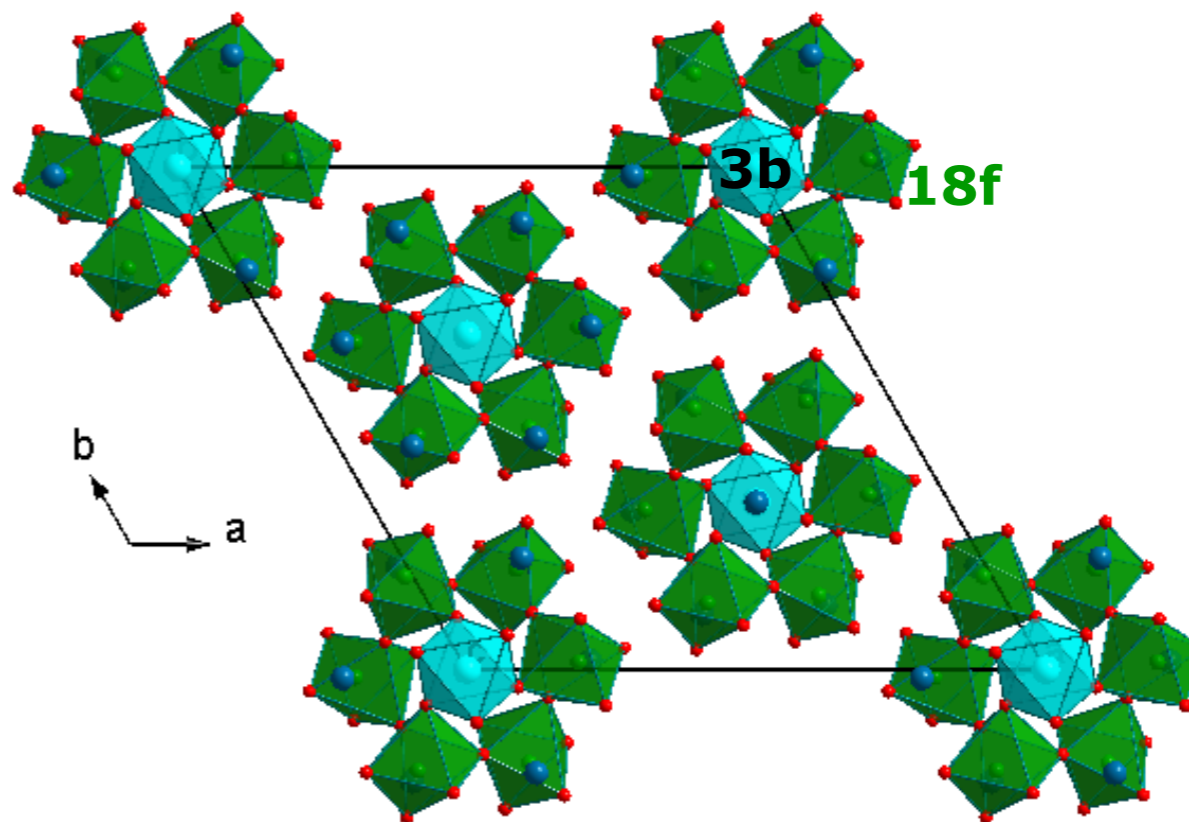
# The 1D $A_7B_7O_{30}$ crystal lattice

Then extended to tungstates in  $La_7W^{6+}_4M^{5+}_3O_{30}$  (M=Nb, Ta)

Space group  $R\bar{3}$



- Synthesized in air
- Nb(Ta) fully on site 3a, partly on site 18f
- $7 B^{+5.57} = 1 Nb^{+5} (3b) + 6 W_{2/3}Nb_{1/3}^{+5.67} (18f)$
- Lower M oxidation state always in octahedron shared by two successive perovskite cages in a row



*F. Goutenoire, S. Kodjikian, E. Suard, J. Solid State Chem. 178 (2005) 2811*

and in  $La_7Mo_{7(2-y)/2}W_{7y/2}O_{30}$  ( $y=0.5, 1.0$ )

*J.E.Vega-Castillo, U.K. Ravella, G. Corbel, P. Lacorre, A. Caneiro, Dalton Trans. 43 (2014) 2661*

# The 1D $A_7B_7O_{30}$ crystal lattice

Further extension to  $La_7W_{7-x}M^{m+}_xO_{30}$  with  $x=3/(6-m)$

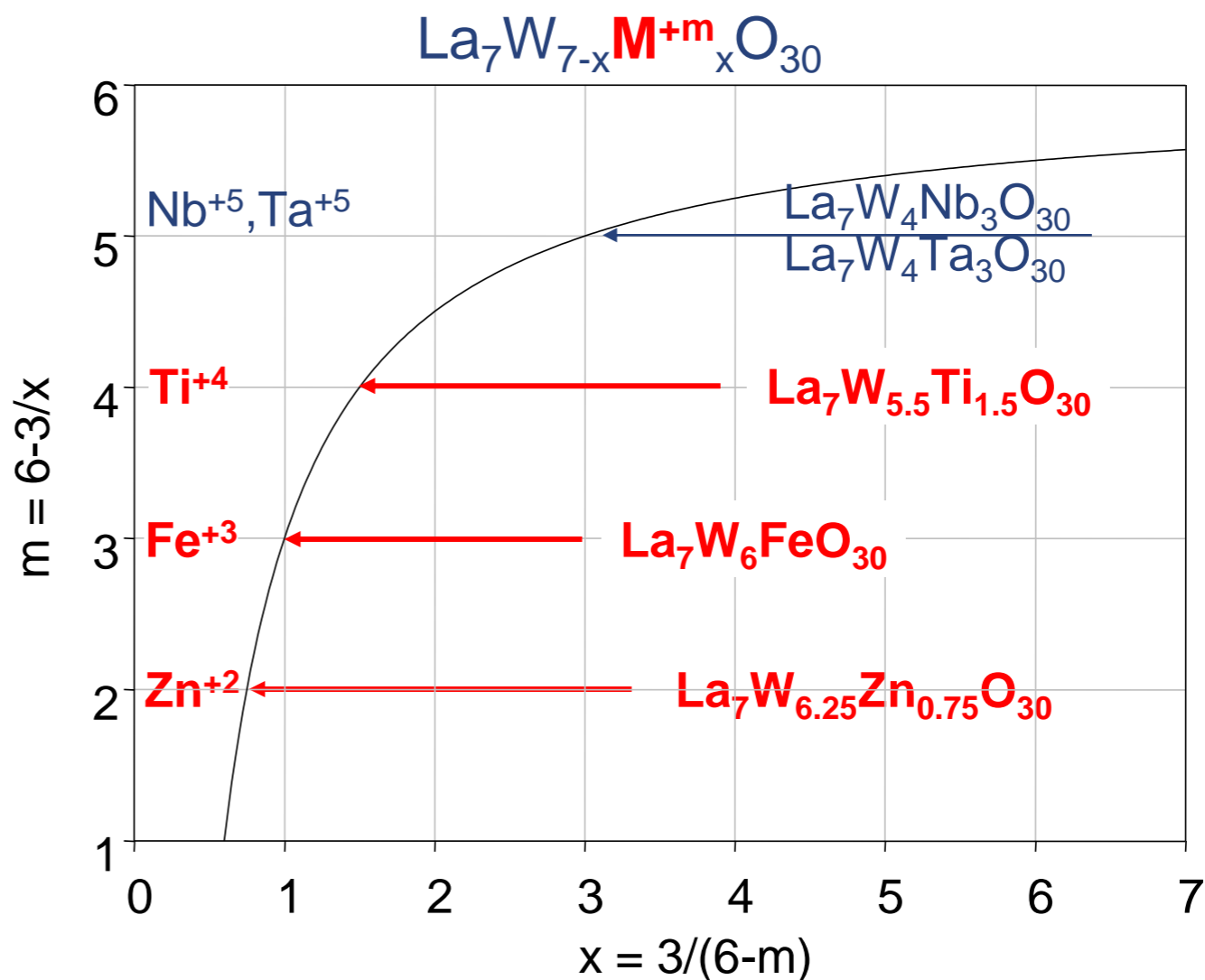
- Sticking to the  $La_7B_7O_{30}$  stoichiometry with tungsten partial substitution by lower valence transition metals :

- When  $m \downarrow$ , then  $x \downarrow$

tetravalent Ti

trivalent Fe

divalent Zn



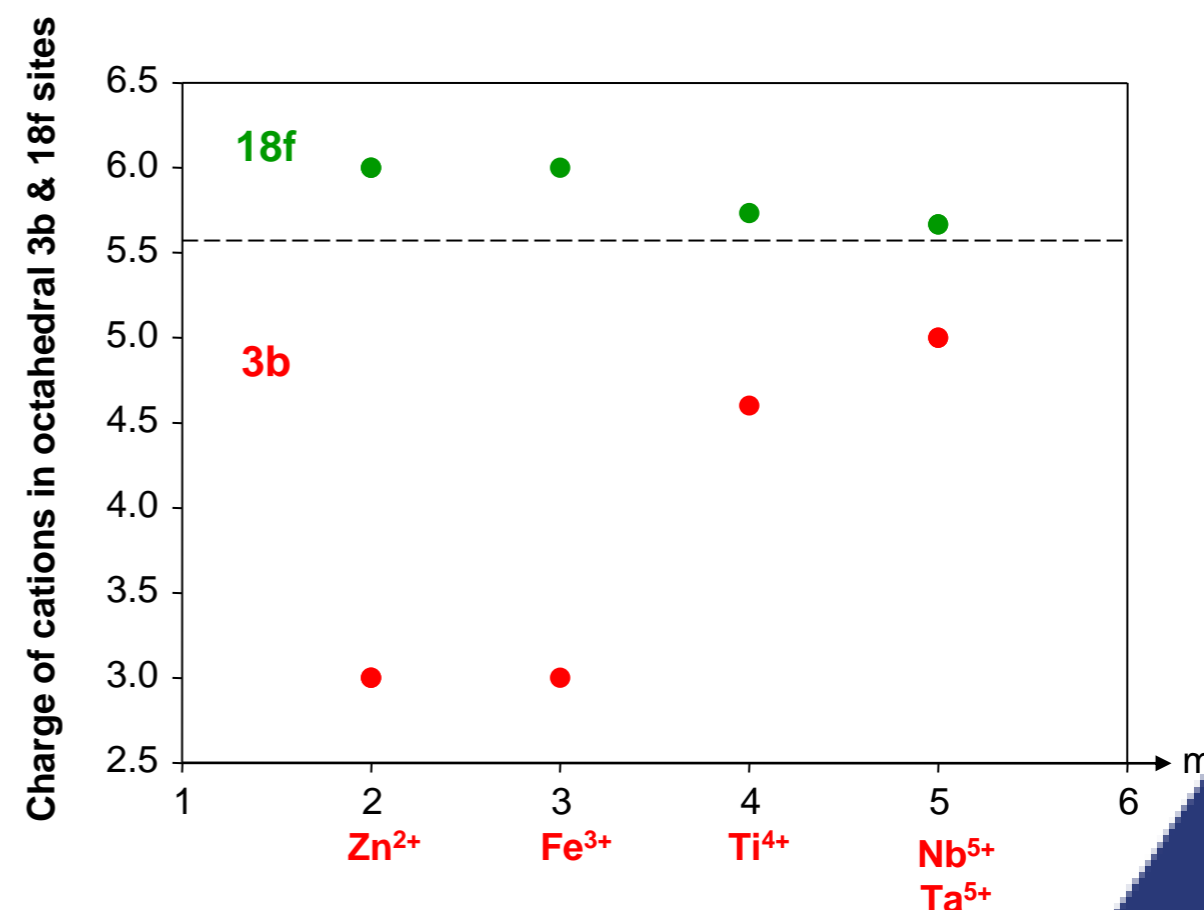
*P. Lacorre, G. Corbel, Inorg. Chem. 58 (2019) 4289*

# The 1D $A_7B_7O_{30}$ crystal lattice

Further extension to  $La_7W_{7-x}M^{m+}_xO_{30}$  with  $x=3/(6-m)$

- Sticking to the  $La_7B_7O_{30}$  stoichiometry with tungsten partial substitution by lower valence transition metals :

$M^{m+}$	3b	18f	$B^{6+}$
$Mo^{5+}/Mo^{4+}$	50%/50%-0%	25%/0%-75%	$Mo^{6+}$
$Nb(Ta)^{5+}$	100%-0%	33.3%-66.7%	$W^{6+}$
$Ti^{4+}$	70%-30%	13.3%-86.7%	$W^{6+}$
<b><math>Fe^{3+}</math></b>	<b>100%-0%</b>	<b>0%-100%</b>	<b><math>W^{6+}</math></b>
$Zn^{2+}$	75%-25%	0%-100%	$W^{6+}$



The only fully ordered compound  
of the whole series

# The 1D $A_7B_7O_{30}$ crystal lattice

## The ordered structure of $La_7W_6FeO_{30}$

Space Group  $R\bar{3}$

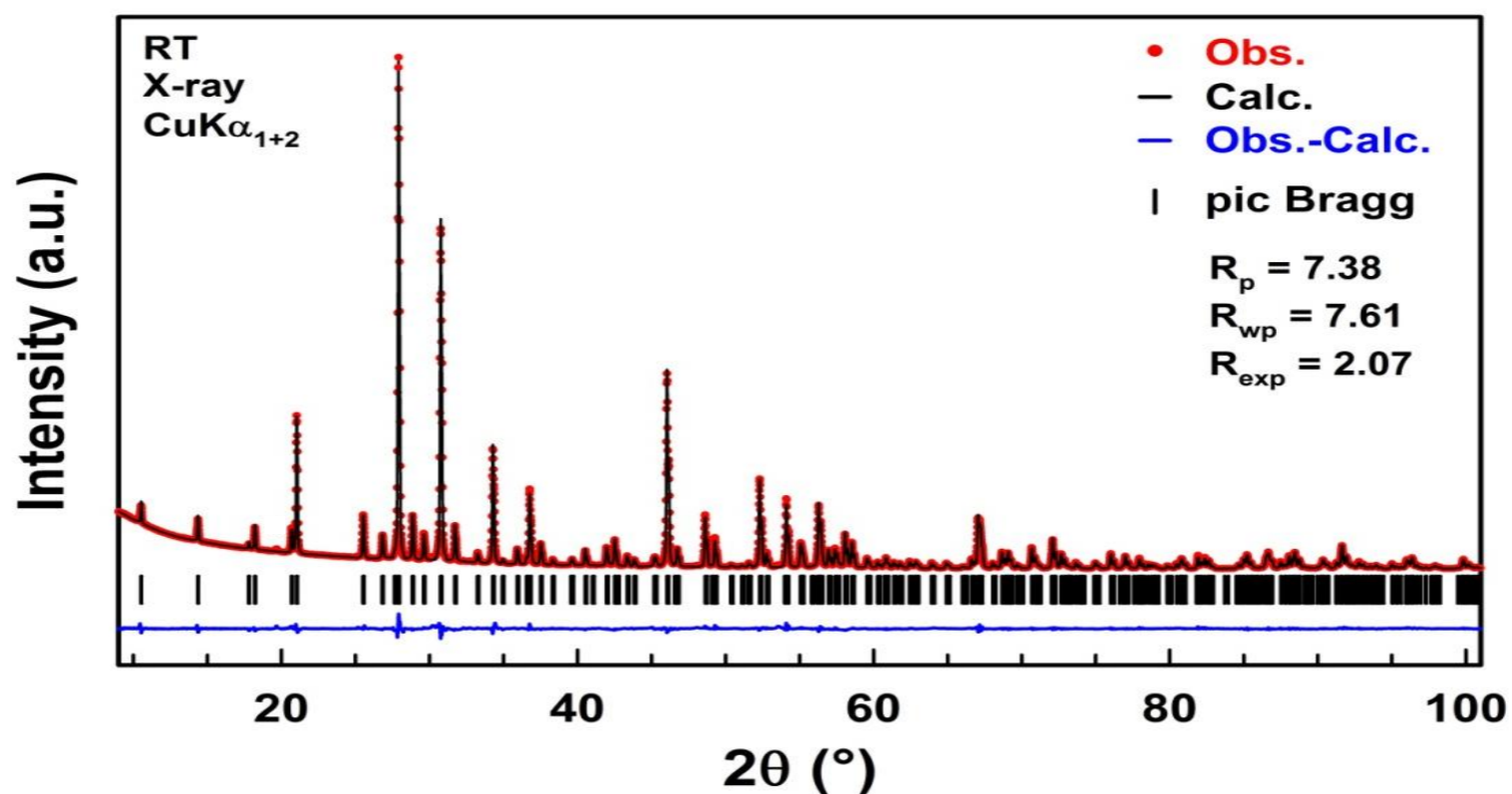
Hexagonal cell :

$a = 16.9635(2) \text{ \AA}$

$c = 6.8460(1) \text{ \AA}$

**X-Ray powder diffraction**  
**Rietveld refinement (FullProf)**

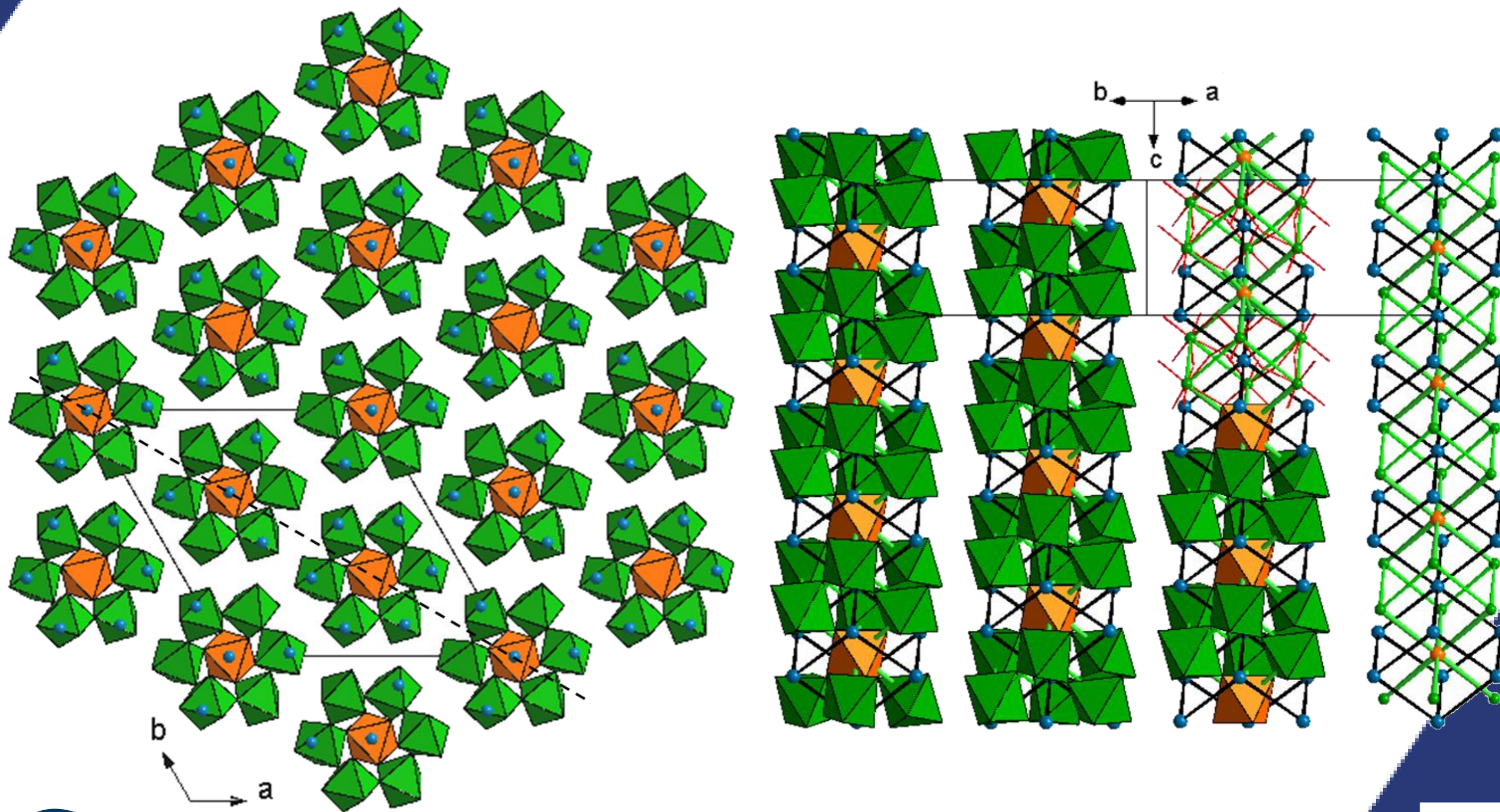
Atom	Site	x	y	z	B( $\text{\AA}^2$ )
La1	3a	0	0	0	0.46(5)
La2	18f	0.7813(2)	0.9853(2)	0.3375(5)	0.46(5)
Fe	3b	0	0	0.5	0.04(3)
W	18f	0.1969(1)	0.0130(1)	0.1695(4)	0.04(3)
O1	18f	0.247(1)	0.098(2)	0.355(4)	1.0(2)
O2	18f	0.295(2)	0.049(2)	0.996(4)	1.0(2)
O3	18f	0.174(1)	0.115(2)	0.042(4)	1.0(2)
O4	18f	0.208(2)	0.928(2)	0.331(3)	1.0(2)
O5	18f	0.031(2)	0.106(1)	0.322(3)	1.0(2)



# The 1D $A_7B_7O_{30}$ crystal lattice

The ordered structure of  $La_7W_6FeO_{30}$

1)



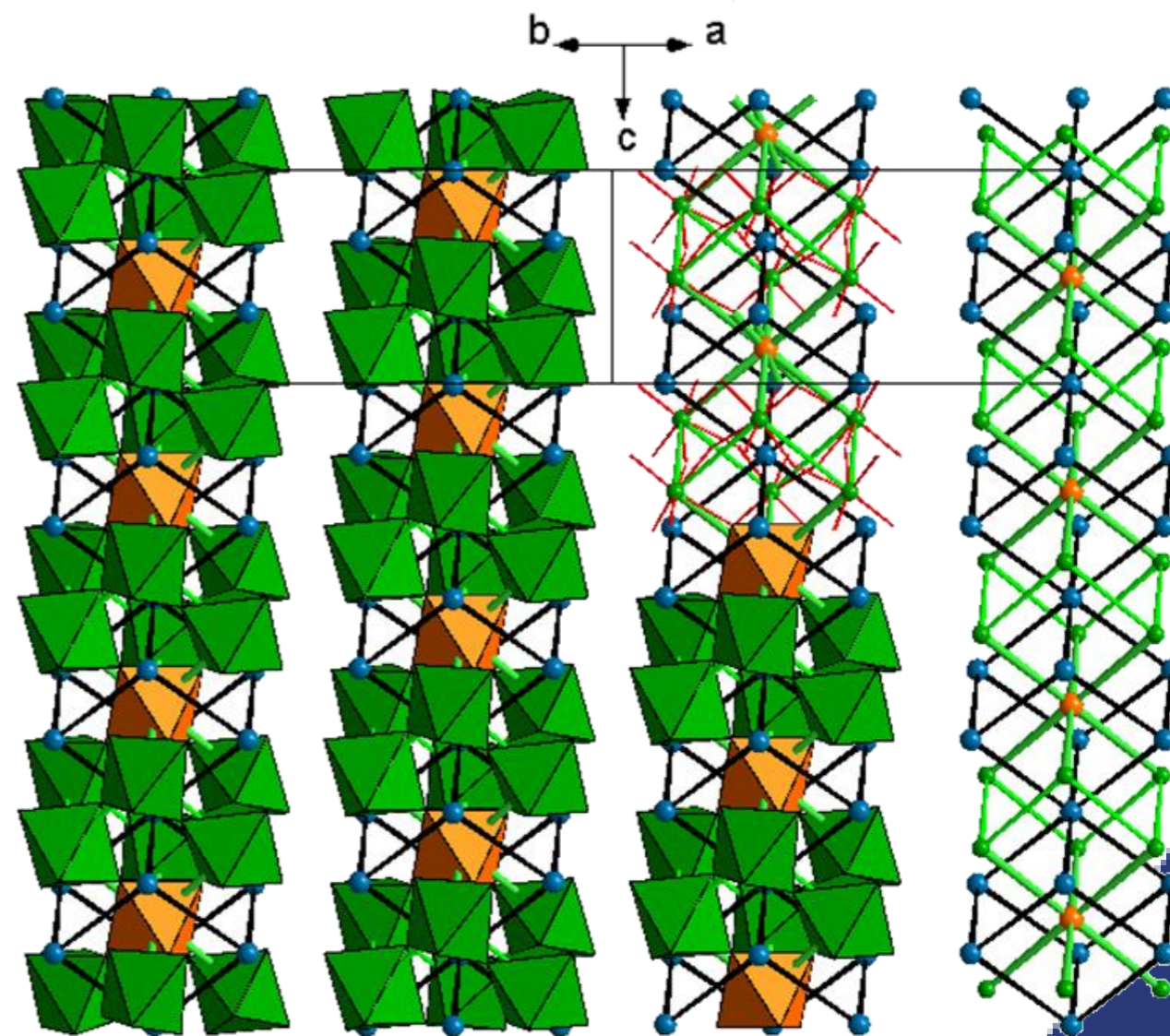
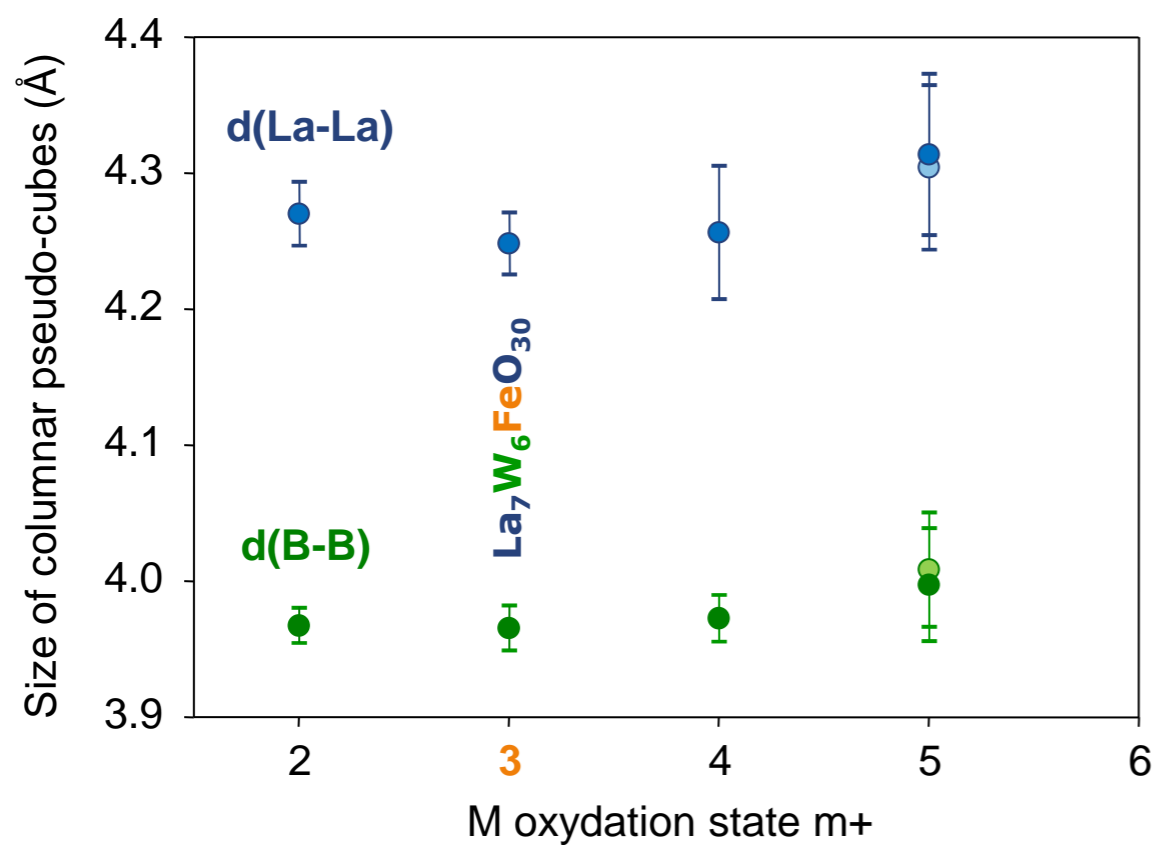


# The 1D $A_7B_7O_{30}$ crystal lattice

The ordered structure of  $La_7W_6FeO_{30}$

1)

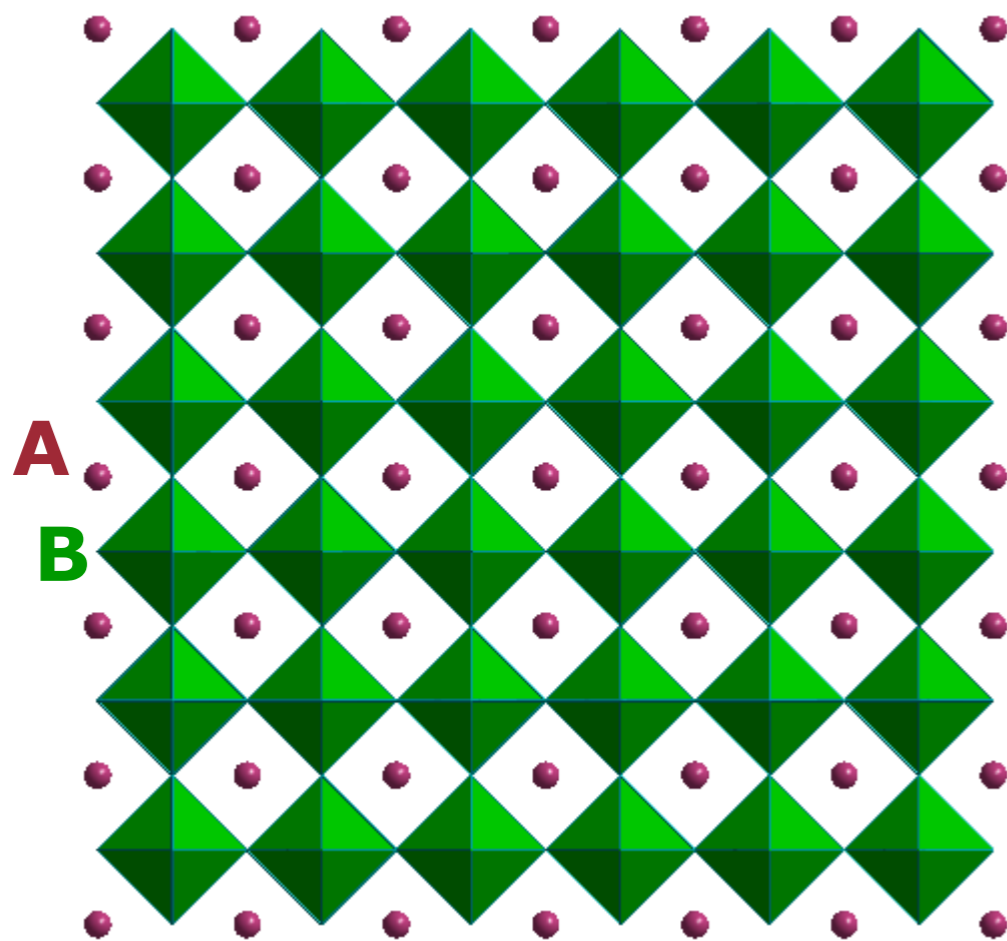
$[A_8]$  and  $[B_8]$  pseudo-cubes sizes



# Oxygen excess in $ABO_{3+\delta}$ type perovskites

General overview: from 3D to 2D

- The perovskite structure can withstand oxygen surstoichiometry up to a certain level while retaining typical perovskite features :



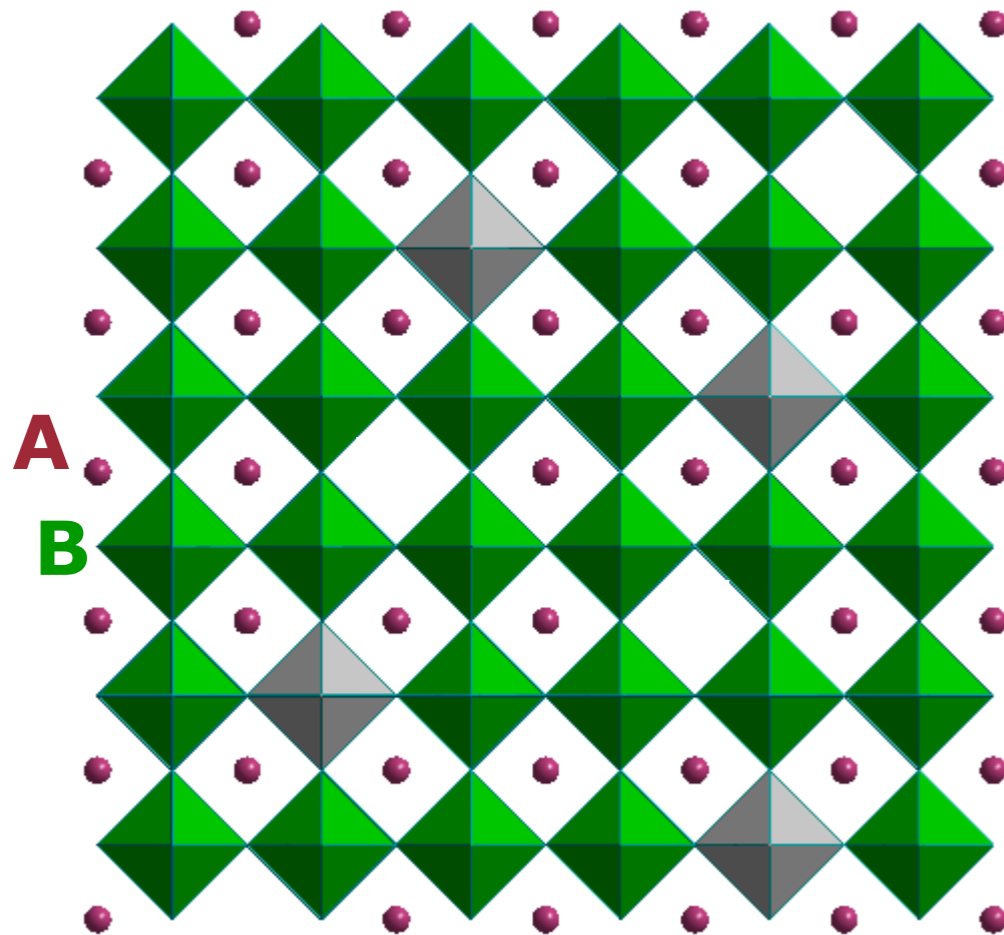
3D configuration  
regular

Regular cubic (or distorted)  
3D arrangement :  
Ordered and stoichiometric  
 $ABO_3$

# Oxygen excess in $ABO_{3+\delta}$ type perovskites

## General overview: from 3D to 2D

- The perovskite structure can withstand oxygen surstoichiometry up to a certain level while retaining typical perovskite features :



**3D configuration  
statistical**

Lacunar  
3D arrangement :  
Oxygen excess  $ABO_{3+\delta}$   
often due to  
cation deficiency,  
as in  $La_{1-x}Mn_{1-x}O_3$   
with  $x = \delta / (3 + \delta)$

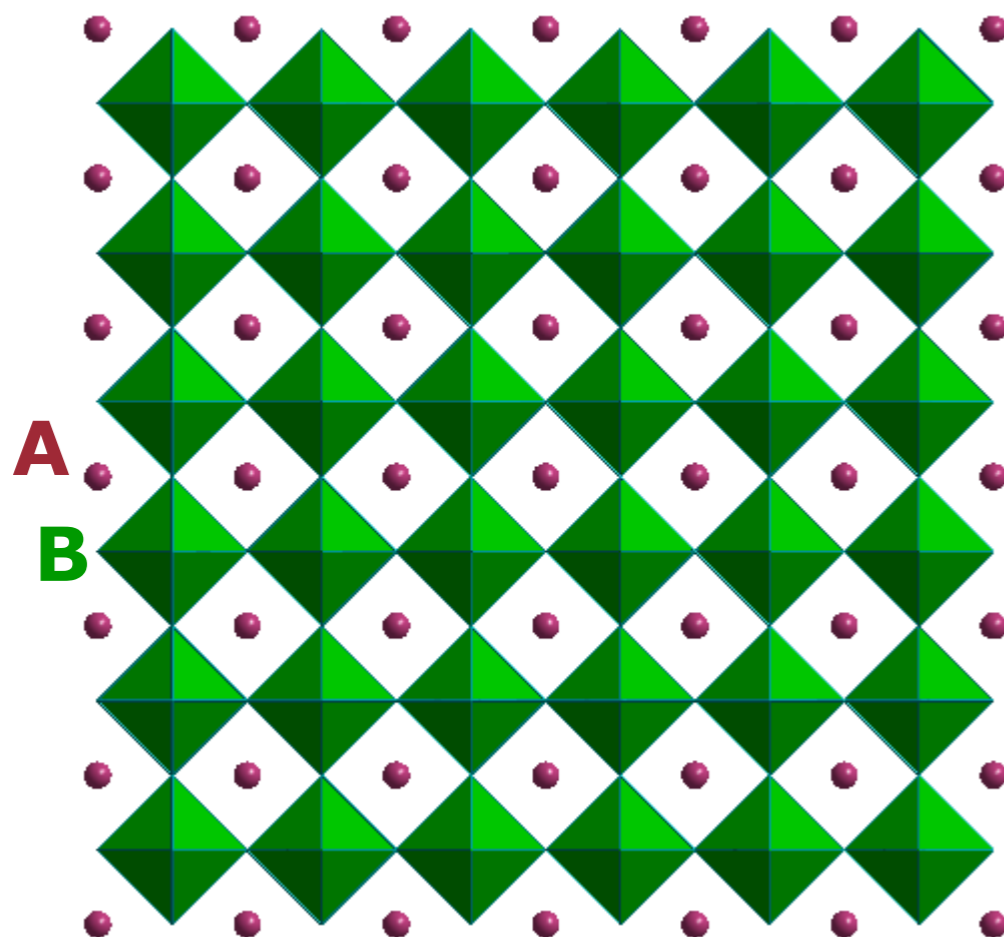
**up to  $\delta \sim 0.4$**

# Oxygen excess in $ABO_{3+\delta}$ type perovskites

## General overview: from 3D to 2D

- The perovskite structure can withstand oxygen surstoichiometry up to a certain level while retaining typical perovskite features :

### 3D configuration



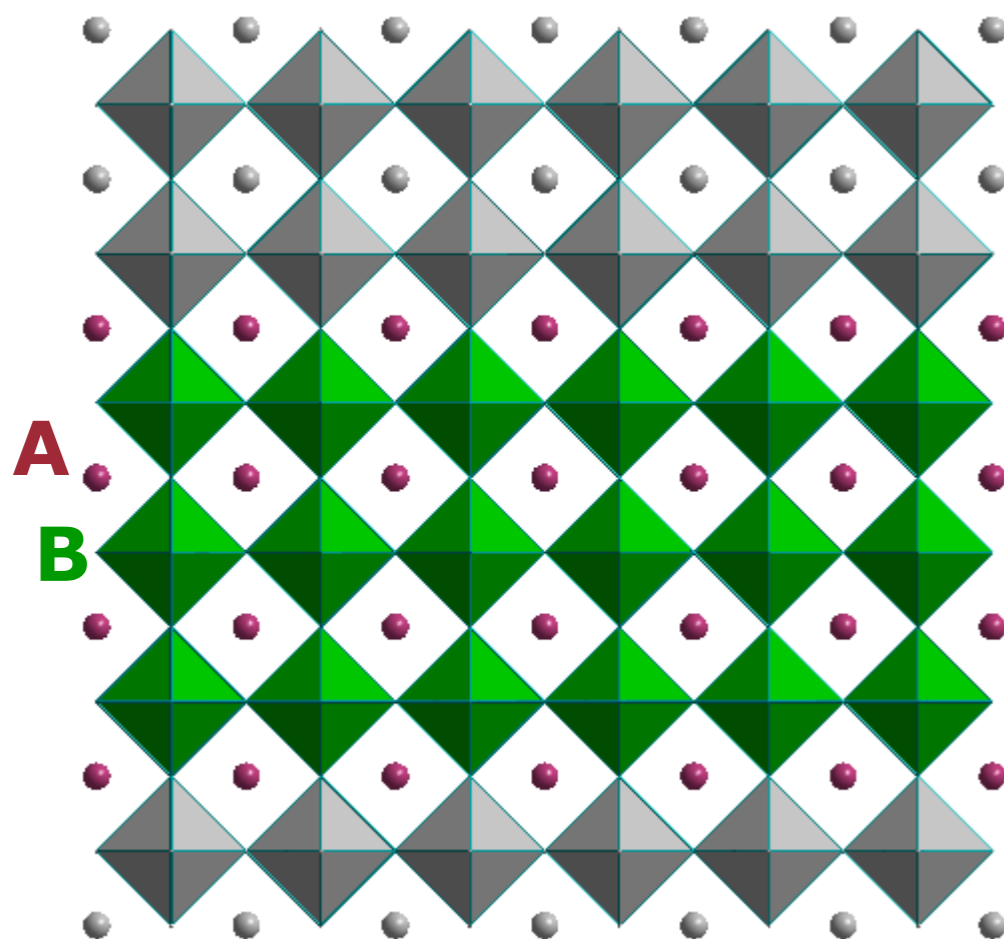
### Regular perovskite

# Oxygen excess in $ABO_{3+\delta}$ type perovskites

## General overview: from 3D to 2D

- The perovskite structure can withstand oxygen surstoichiometry up to a certain level while retaining typical perovskite features :

### 3D configuration



### Regular perovskite

### 2D configuration

Higher values of oxygen excess are possible, at the expense of tridimensionality:

#### 1) In the Dion-Jacobson series



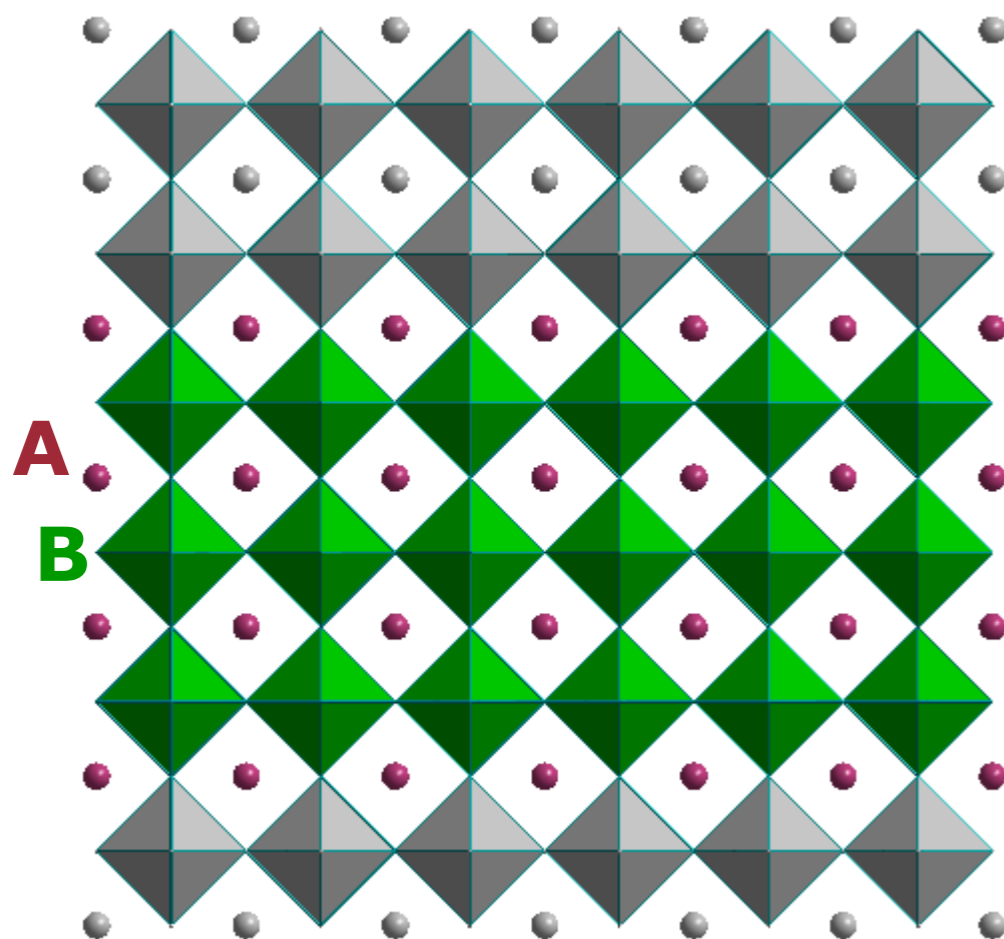
2D slabs of  $k$  octahedral planes isolated from each other

# Oxygen excess in $ABO_{3+\delta}$ type perovskites

General overview: from 3D to 2D

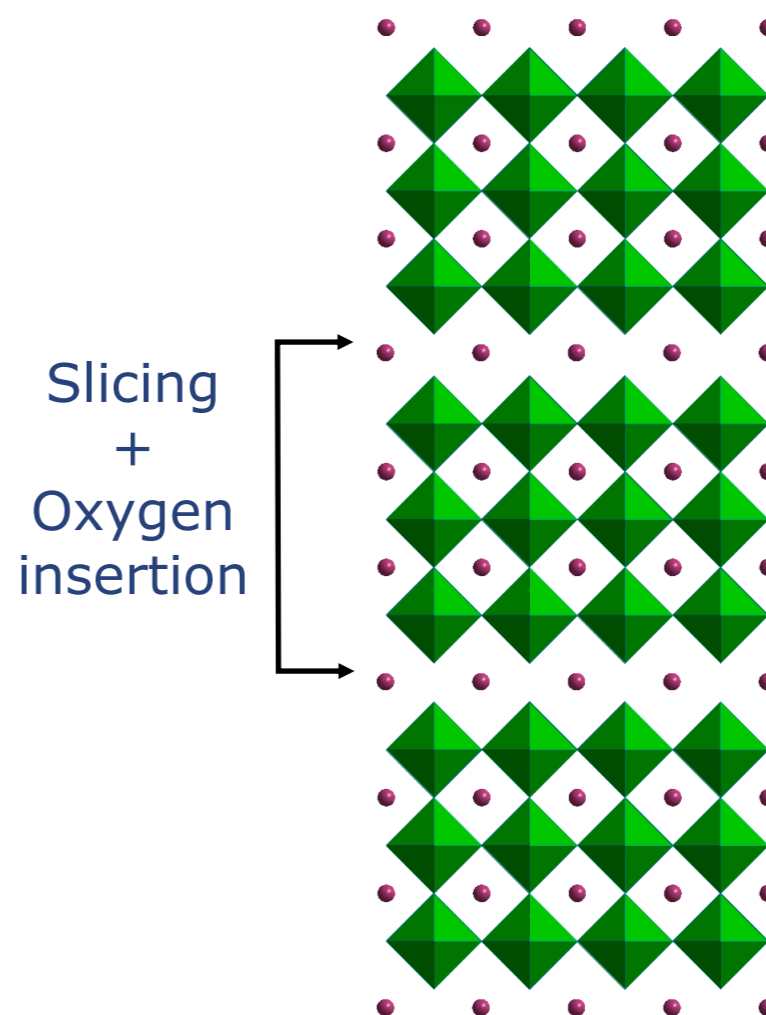
- The perovskite structure can withstand oxygen surstoichiometry up to a certain level while retaining typical perovskite features :

3D configuration



Regular perovskite

2D configuration



Dion-Jacobson series  
 $A_k B_k O_{3k+1}$  (here  $k=3$ )



$\delta = 1/k$

up to

$\delta = 0.5$

for  $k=2$

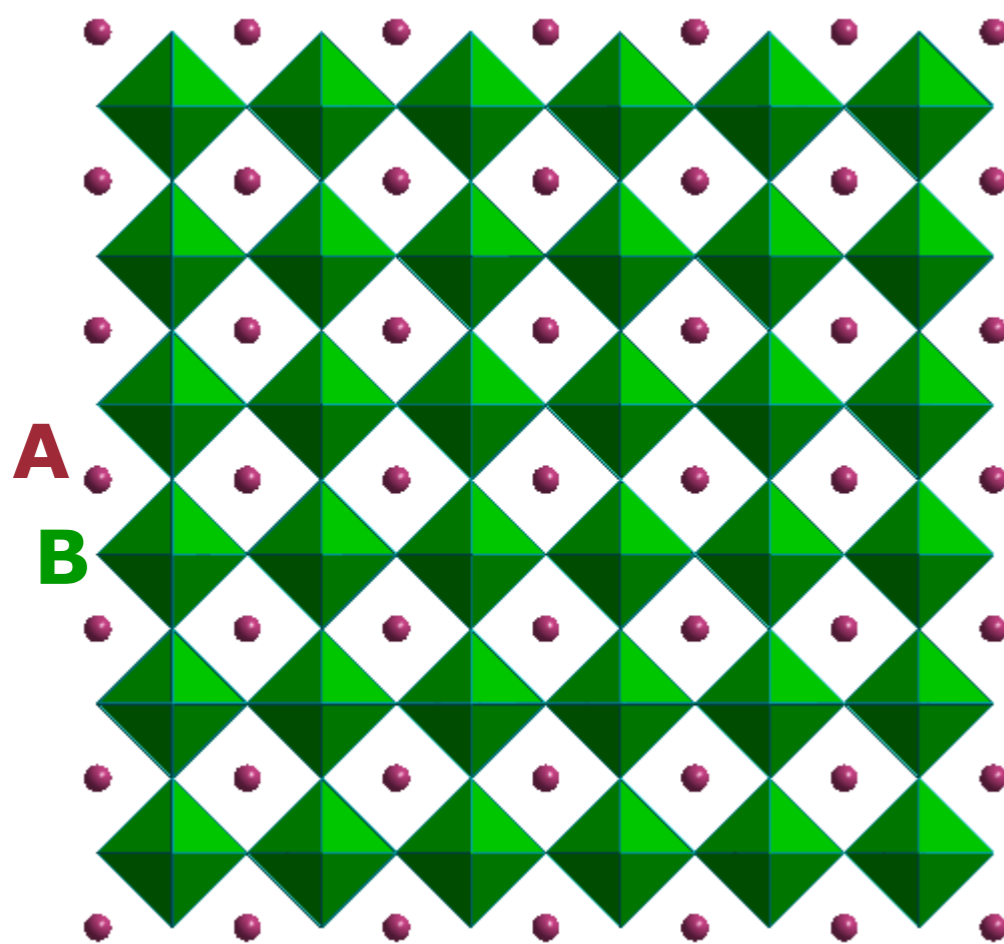
( $BaSrTa_2O_7$ )

# Oxygen excess in $ABO_{3+\delta}$ type perovskites

General overview: from 3D to 2D

- The perovskite structure can withstand oxygen surstoichiometry up to a certain level while retaining typical perovskite features :

3D configuration



Regular

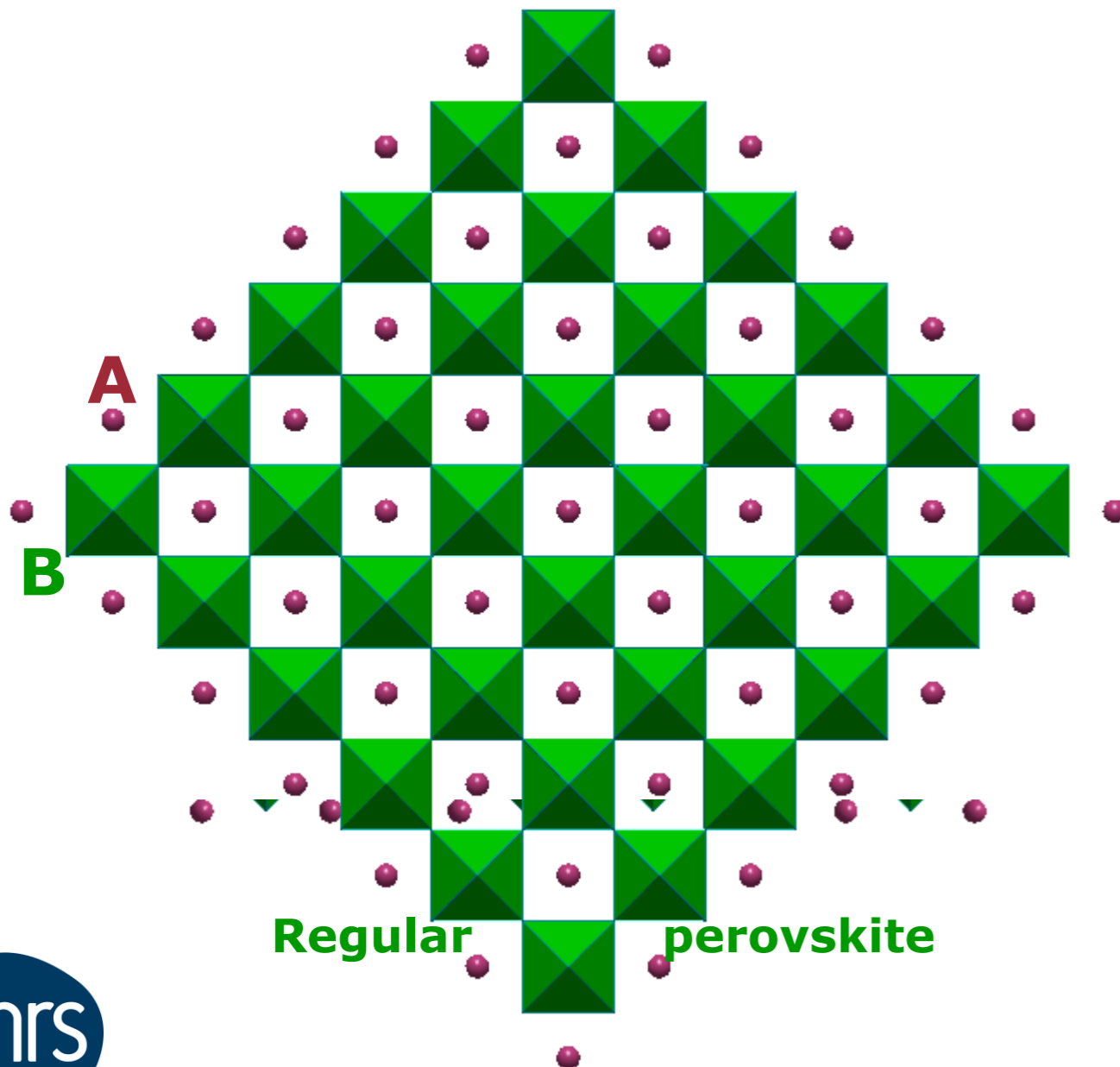
perovskite

# Oxygen excess in $ABO_{3+\delta}$ type perovskites

## General overview: from 3D to 2D

- The perovskite structure can withstand oxygen surstoichiometry up to a certain level while retaining typical perovskite features :

### 3D configuration



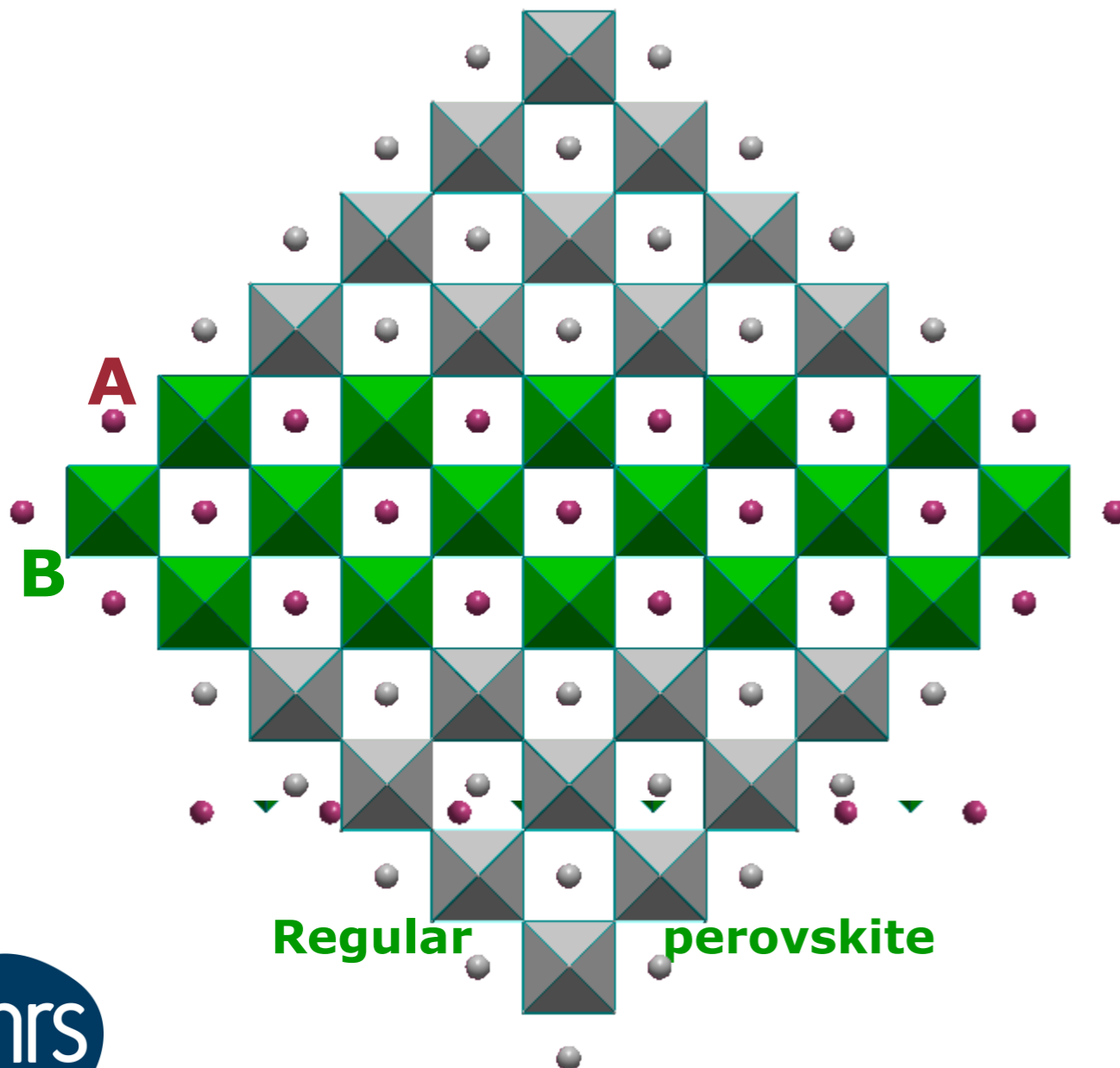


# Oxygen excess in $ABO_{3+\delta}$ type perovskites

## General overview: from 3D to 2D

- The perovskite structure can withstand oxygen surstoichiometry up to a certain level while retaining typical perovskite features :

### 3D configuration

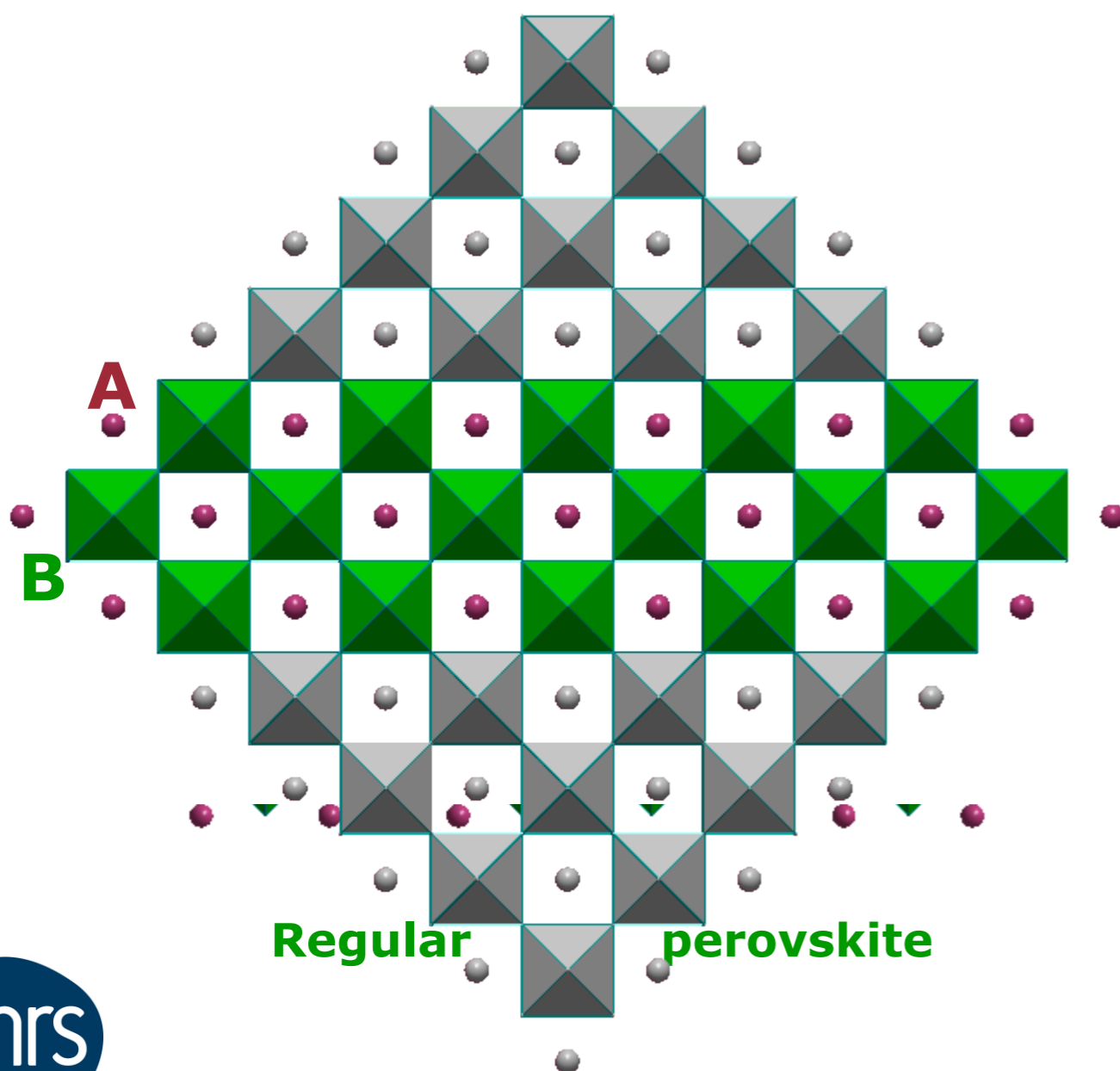


# Oxygen excess in $ABO_{3+\delta}$ type perovskites

## General overview: from 3D to 2D

- The perovskite structure can withstand oxygen surstoichiometry up to a certain level while retaining typical perovskite features :

3D configuration



2D configuration

Higher values of oxygen excess are possible, at the expense of tridimensionality:

2) **In the  $A_nB_nO_{3n+2}$  series**

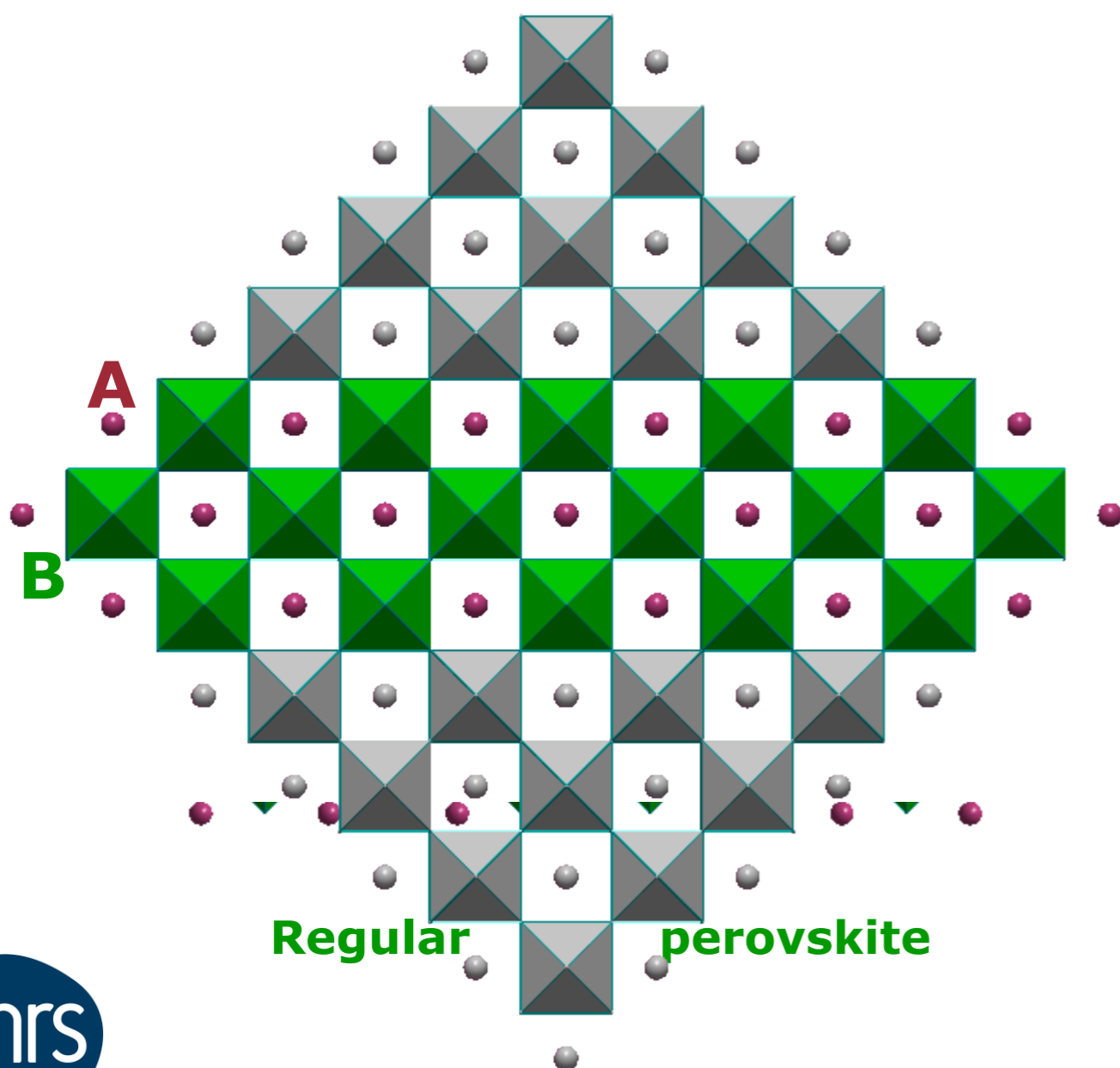
2D slabs of  $n$  octahedra edges isolated from each other

# Oxygen excess in $ABO_{3+\delta}$ type perovskites

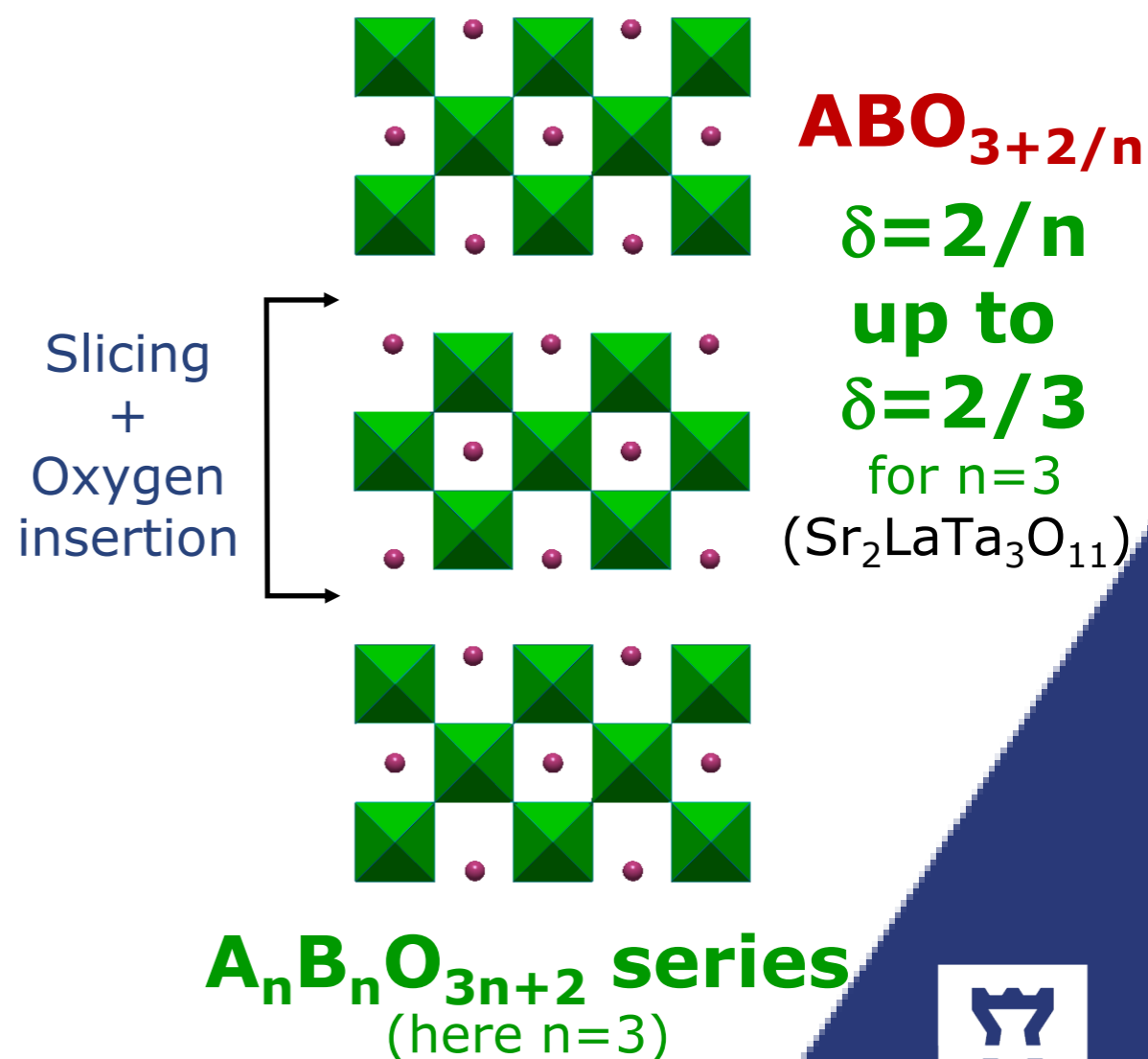
## General overview: from 3D to 2D

- The perovskite structure can withstand oxygen surstoichiometry up to a certain level while retaining typical perovskite features :

3D configuration

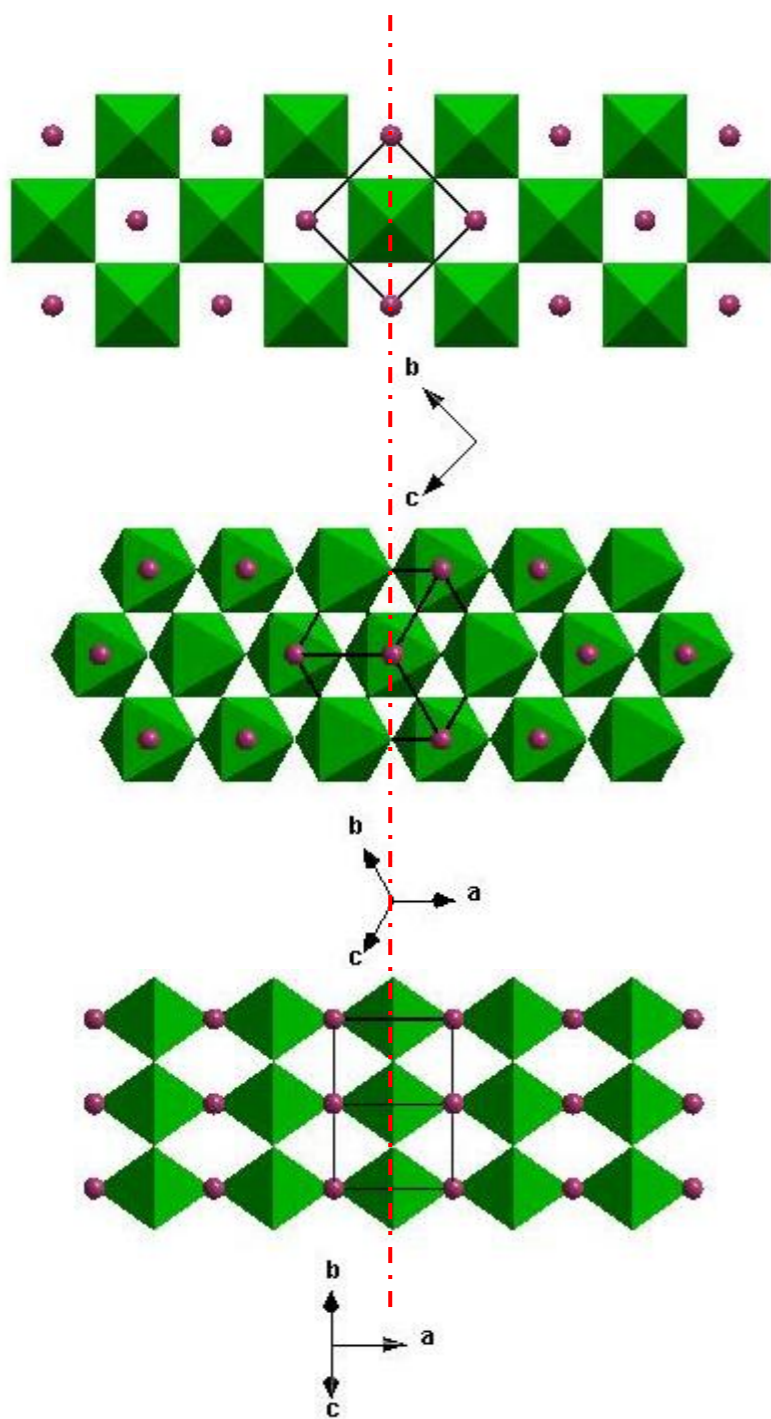


2D configuration



# Oxygen excess in $ABO_{3+\delta}$ type perovskites

$A_nB_nO_{3n+2}$  series member  $n=3$  :  $A_3B_3O_{11} = ABO_{3.667}$

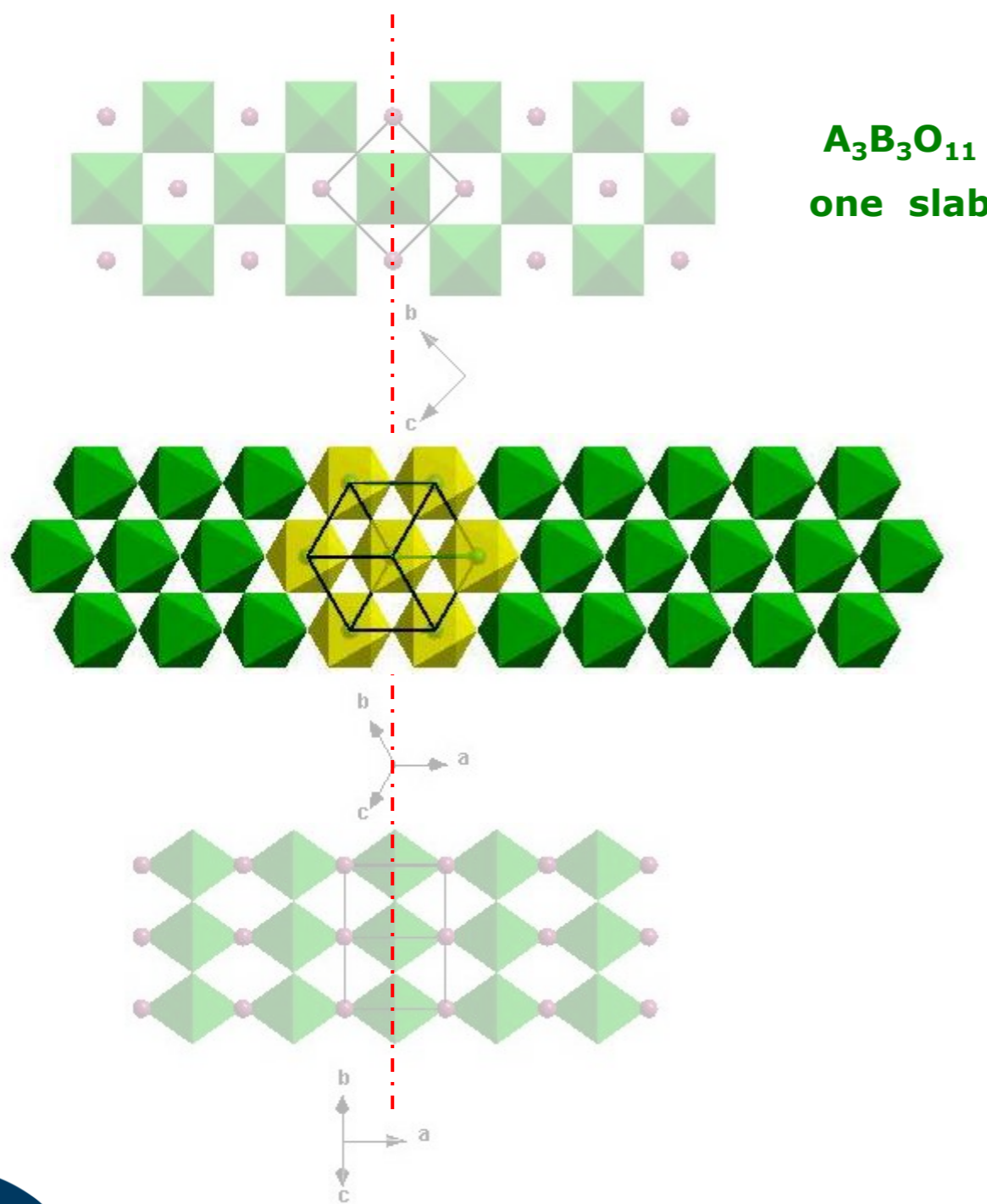


$A_3B_3O_{11}$   
one slab

# Oxygen excess in $ABO_{3+\delta}$ type perovskites

$A_nB_nO_{3n+2}$  series member  $n=3$  :  $A_3B_3O_{11} = ABO_{3.667}$

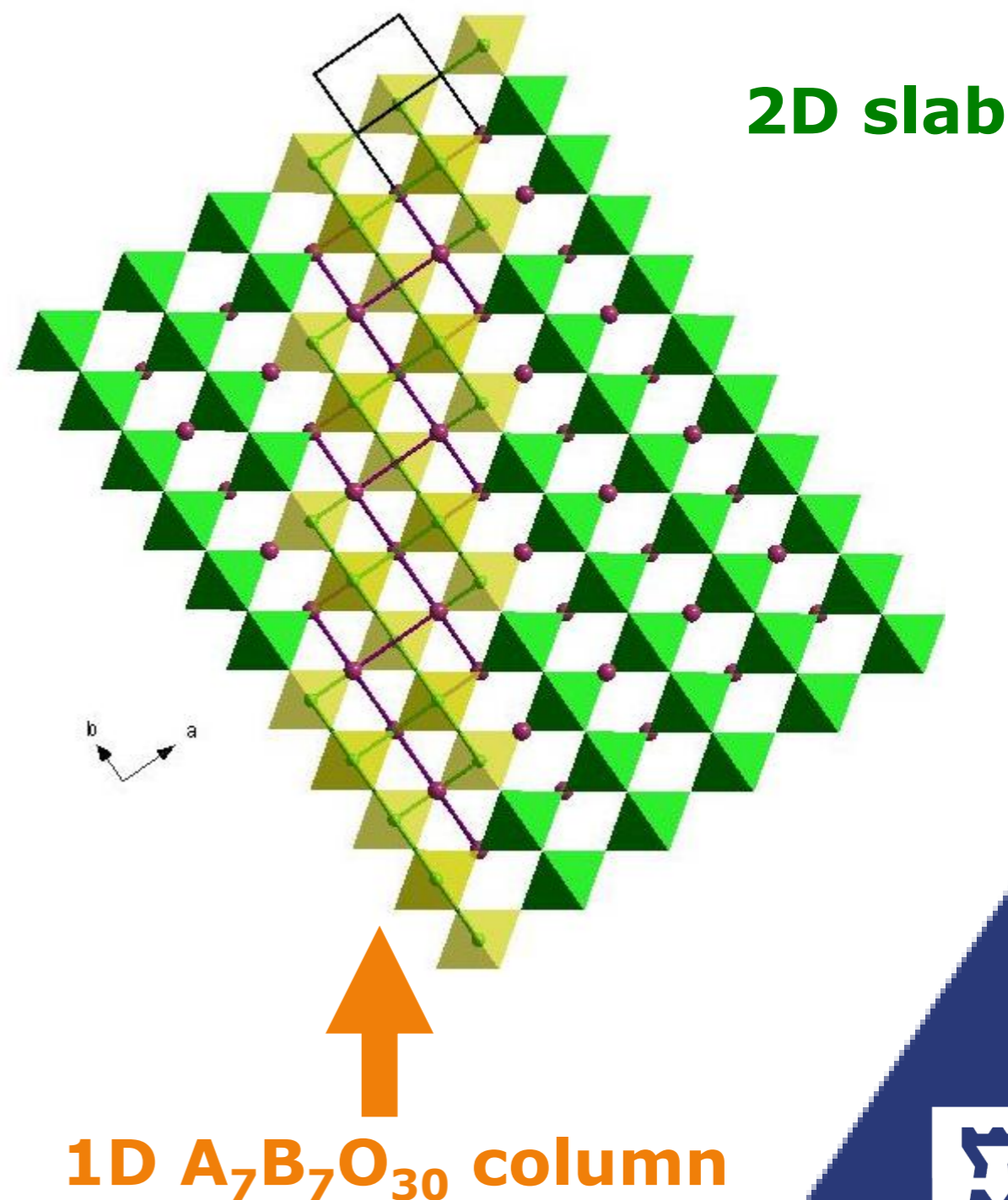
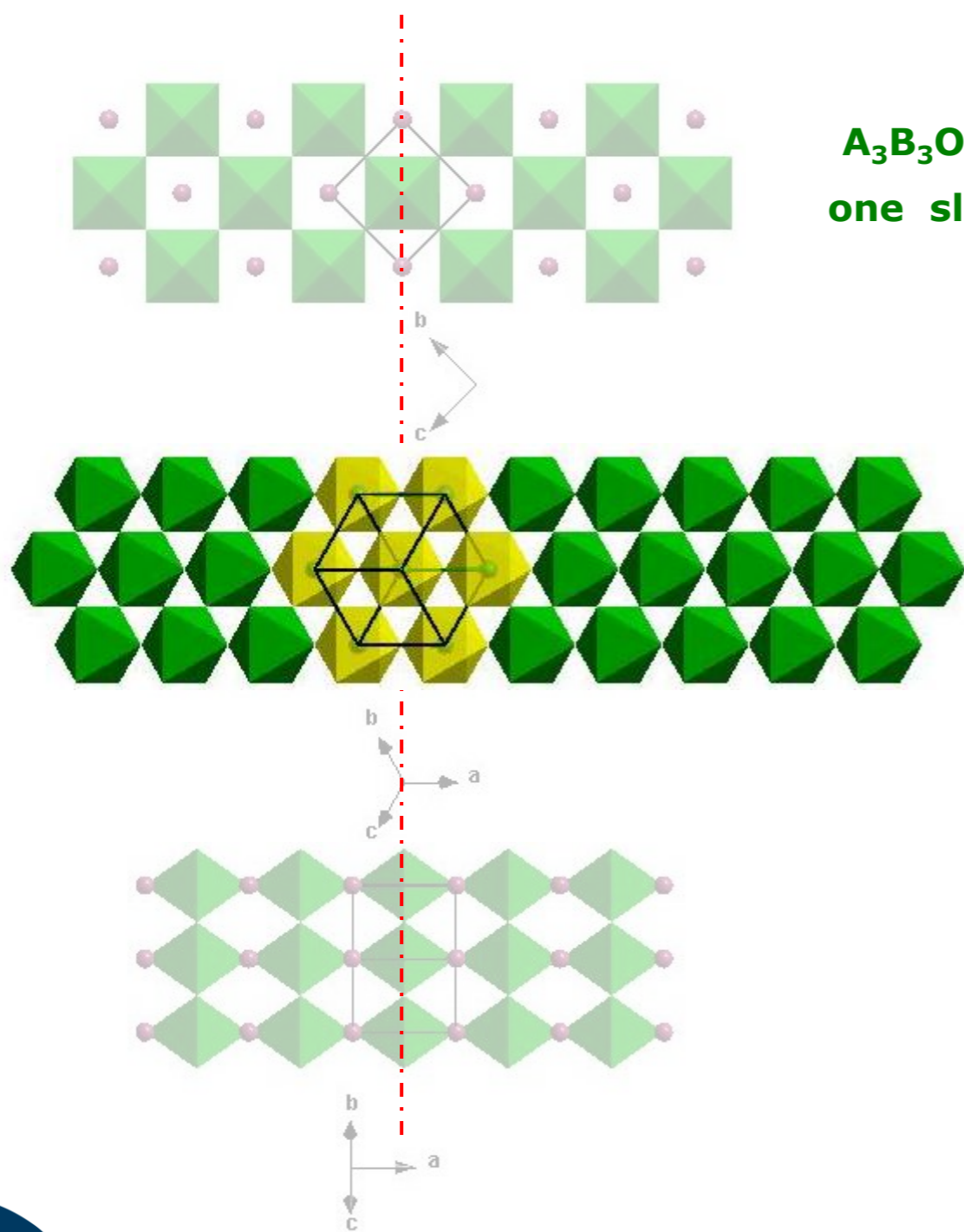
2)



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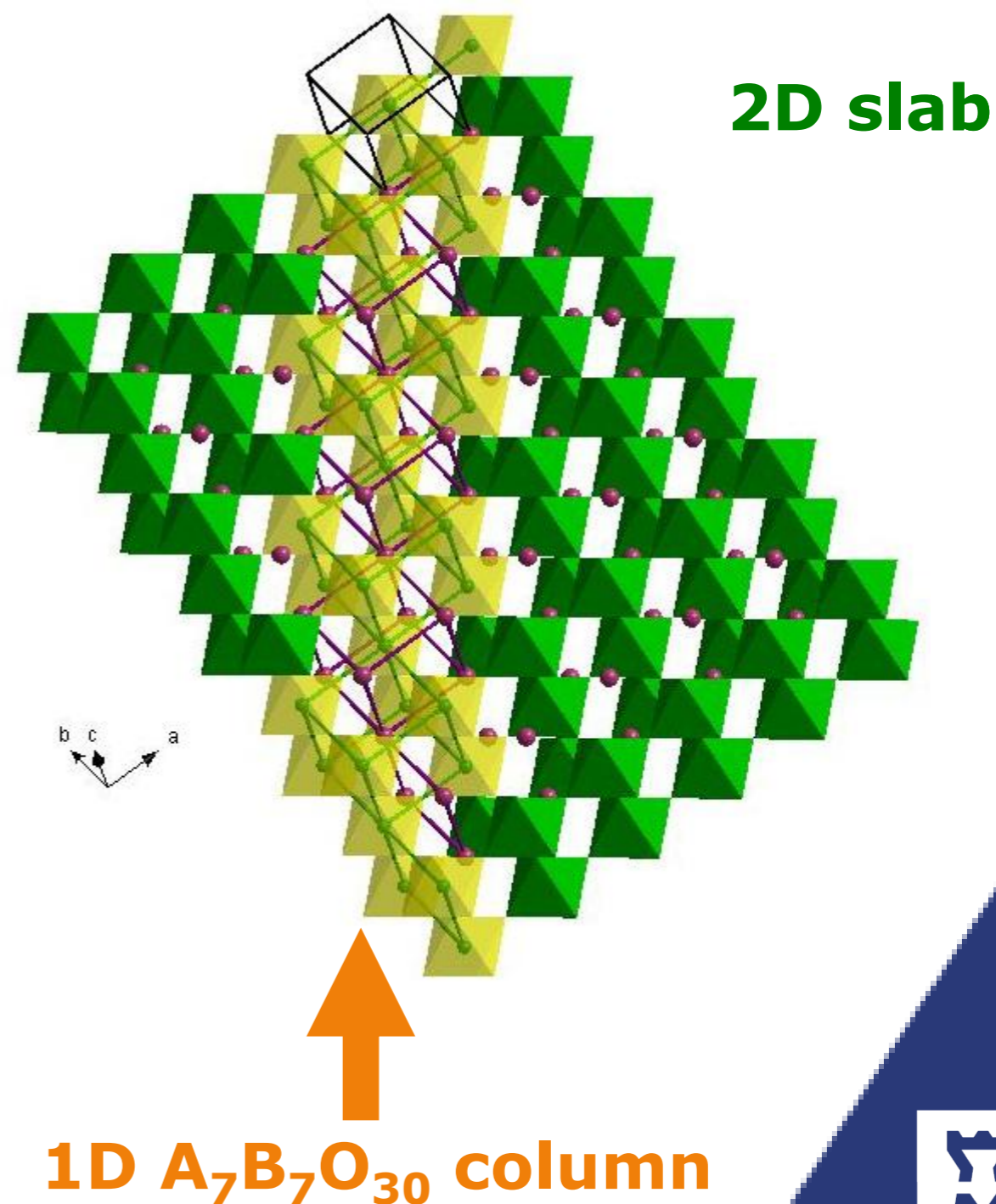
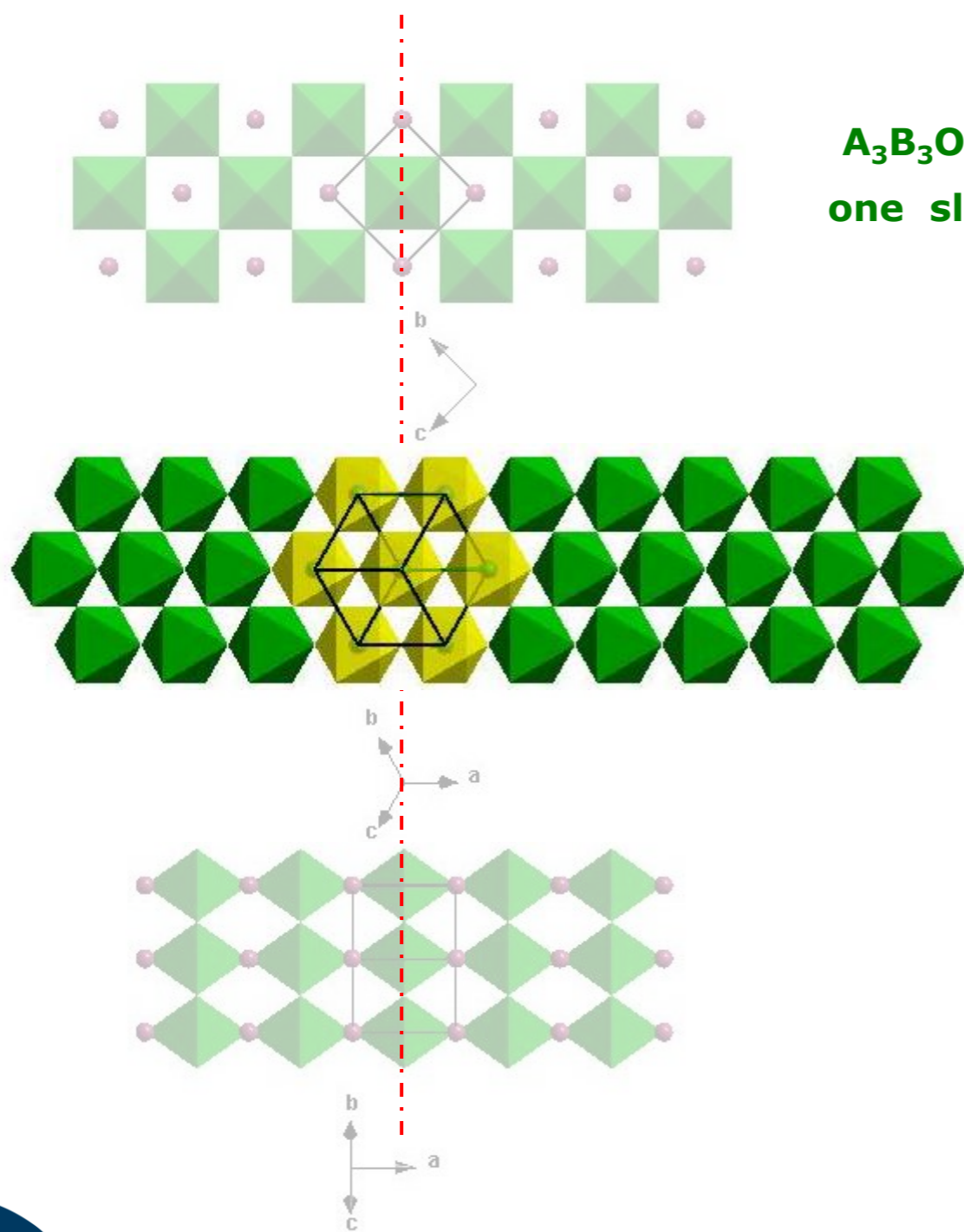
2)



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2)



# Oxygen excess in $ABO_{3+\delta}$ type perovskites

2)

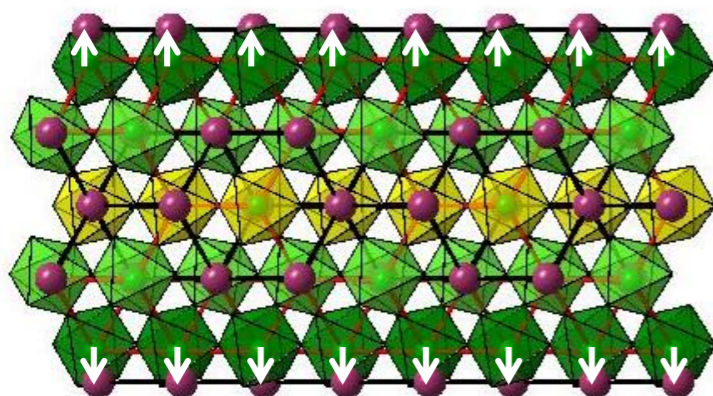
Common features between 2D  $A_nB_nO_{3n+2}$  and 1D  $A_7B_7O_{30}$  series

Dim.	n col/slab thickness	Formula	Octa. distort. % peri-center-peri	Cation charge in octahedra peri-center-peri
$A_7B_7O_{30}$ 1D	1D	$La_7Mo_7O_{30}$	19 - 0 - 19	5.75 - 4.5 - 5.75
	1D	$La_7W_4Ta_3O_{30}$	20 - 0 - 20	5.67 - 5 - 5.67
	1D	$La_7W_{5.5}Ti_{1.5}O_{30}$	20 - 0 - 20	5.73 - 4.6 - 5.73
	1D	$La_7W_6FeO_{30}$	18 - 0 - 18	6 - 3 - 6
	1D	$La_7W_{6.5}Zn_{0.75}O_{30}$	21 - 0 - 21	6 - 3 - 6
$A_nB_nO_{3n+2}$ 2D	2D	$Sr_2LaTa_3O_{11}$	12 - 4 - 12	5 - 5 - 5
	2D	$La_4Ti_4O_{14}$	20-16-16-20	4-4-4-4
	2D	$Sr_4Ta_4O_{14}$	15-9-9-15	5-5-5-5
	2D	$Ca_5Nb_5O_{17}$	23-17-3-17-23	4.97-4.81-4.73-4.81-4.97
	2D	$Ca_5TiNb_4O_{17}$	22-16-1-16-22	4.95-4.8-4.56-4.8-4.95
	2D	$Sr_5TiNb_4O_{17}$	20-16-2-16-20	4.9-4.82-4.56-4.82-4.9
	2D	$La_5FeTi_4O_{17}$	22-17-2-17-22	3.97-3.85-3.53-3.85-3.97
2D	$La_6Fe_2Ti_4O_{20}$	23-17-4-4-17-23	3.95-3.76-3.32-3.32-3.76-3.95	

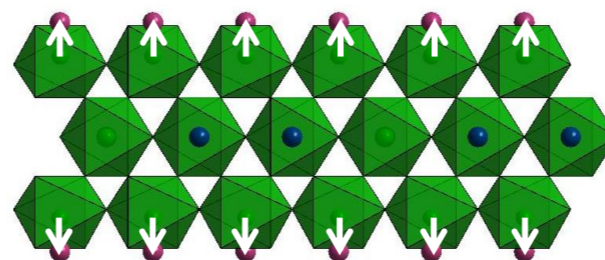
- Common characteristics :
  - both **octahedral distortions** and **B cationic charges** increase from center to outskirts of perovskite slabs/columns;
  - A cations** are shifted out from the slab/column center.



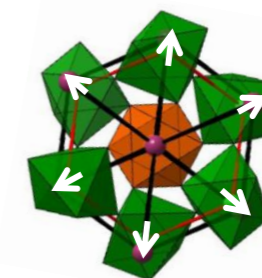
2D, n=5



2D, n=3



1D, n=3

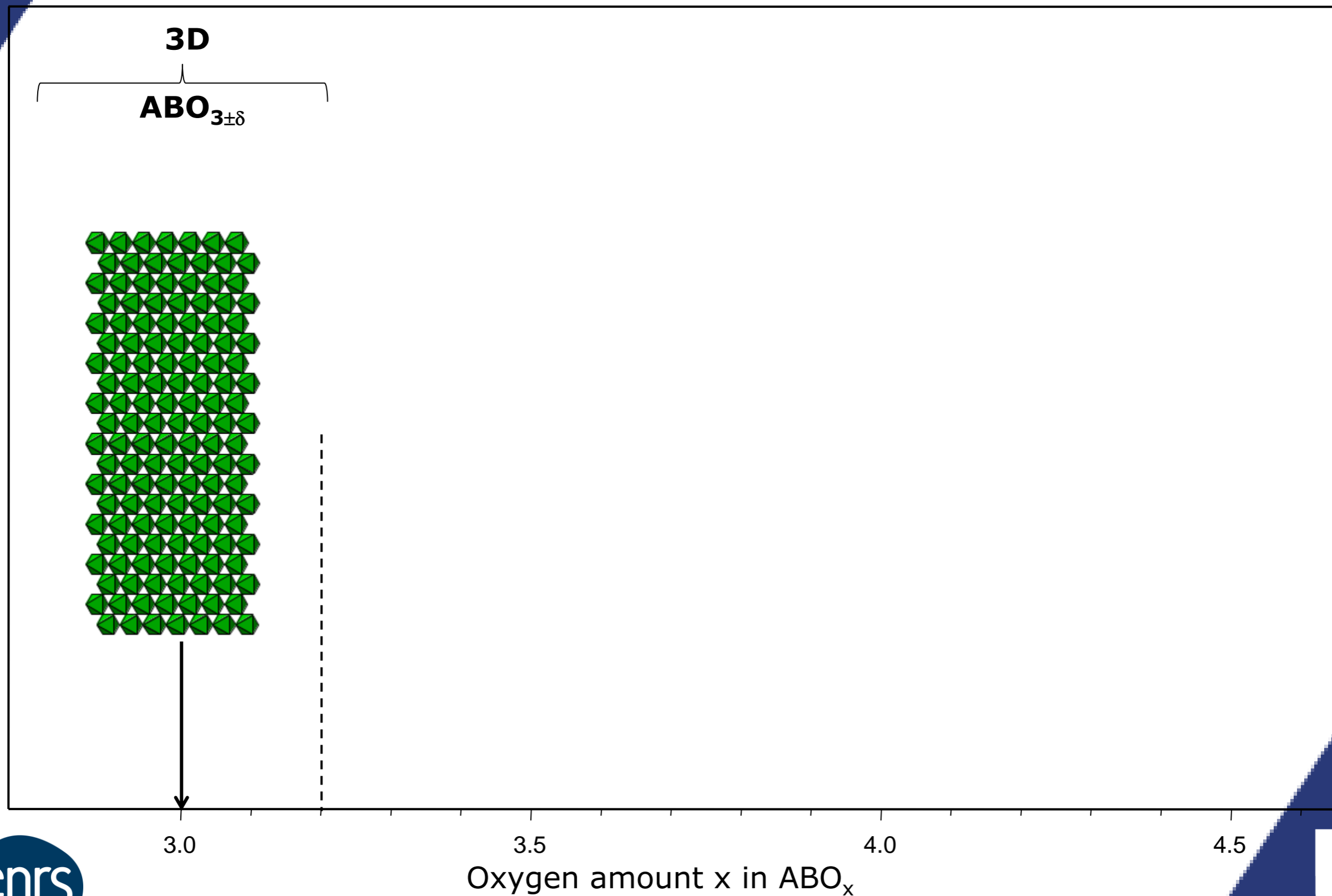




# Oxygen excess in $ABO_{3+\delta}$ type perovskites

2)

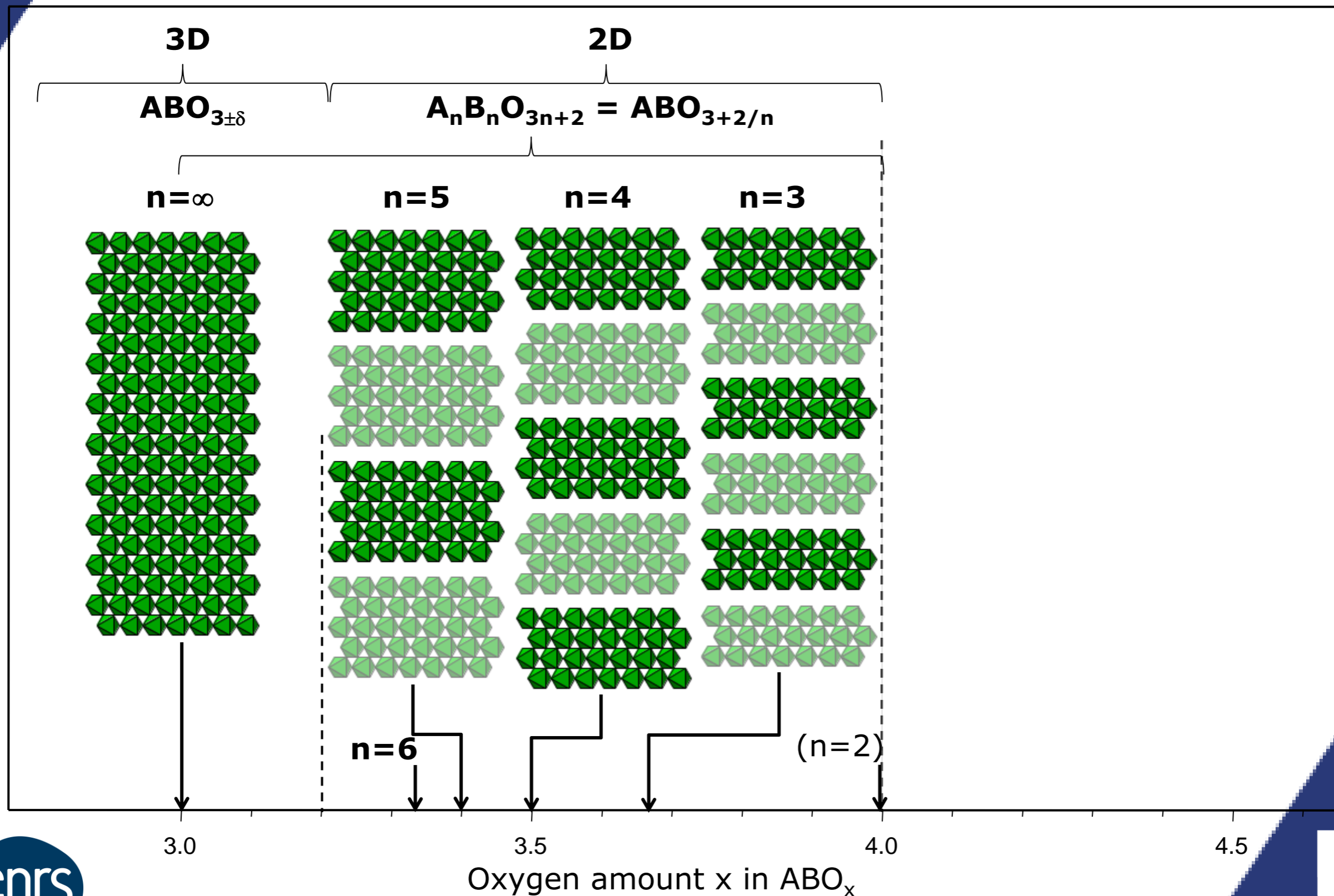
The  $A_n B_n O_{3n+2}$  way



# Oxygen excess in $ABO_{3+\delta}$ type perovskites

2)

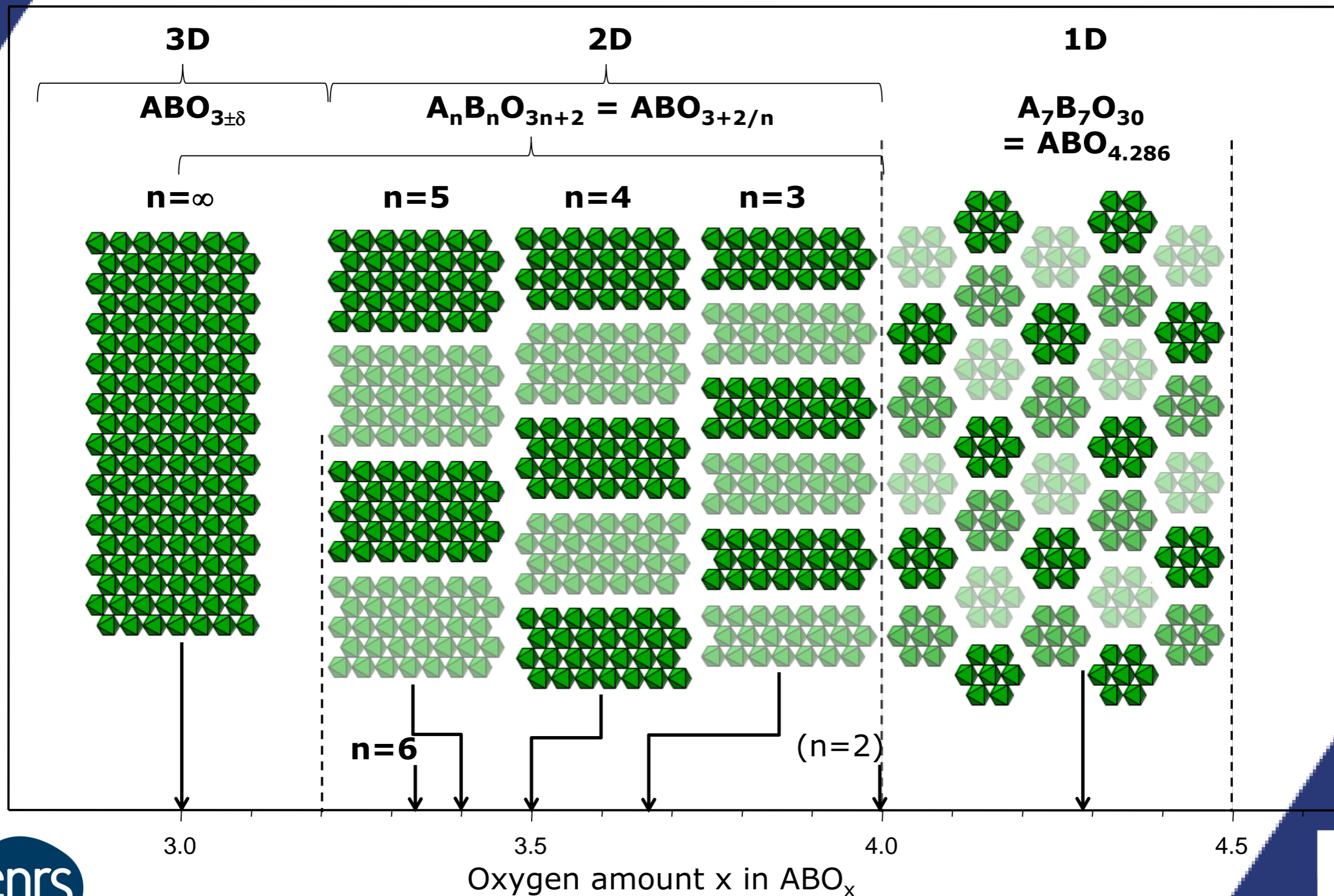
The  $A_n B_n O_{3n+2}$  way



# Oxygen excess in $ABO_{3+\delta}$ type perovskites

2)

The  $A_n B_n O_{3n+2}$  way



# Other members of the $A_7B_7O_{30}$ family: the $MPr_2W_2O_{10}$ case

*Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 3, 711–715*

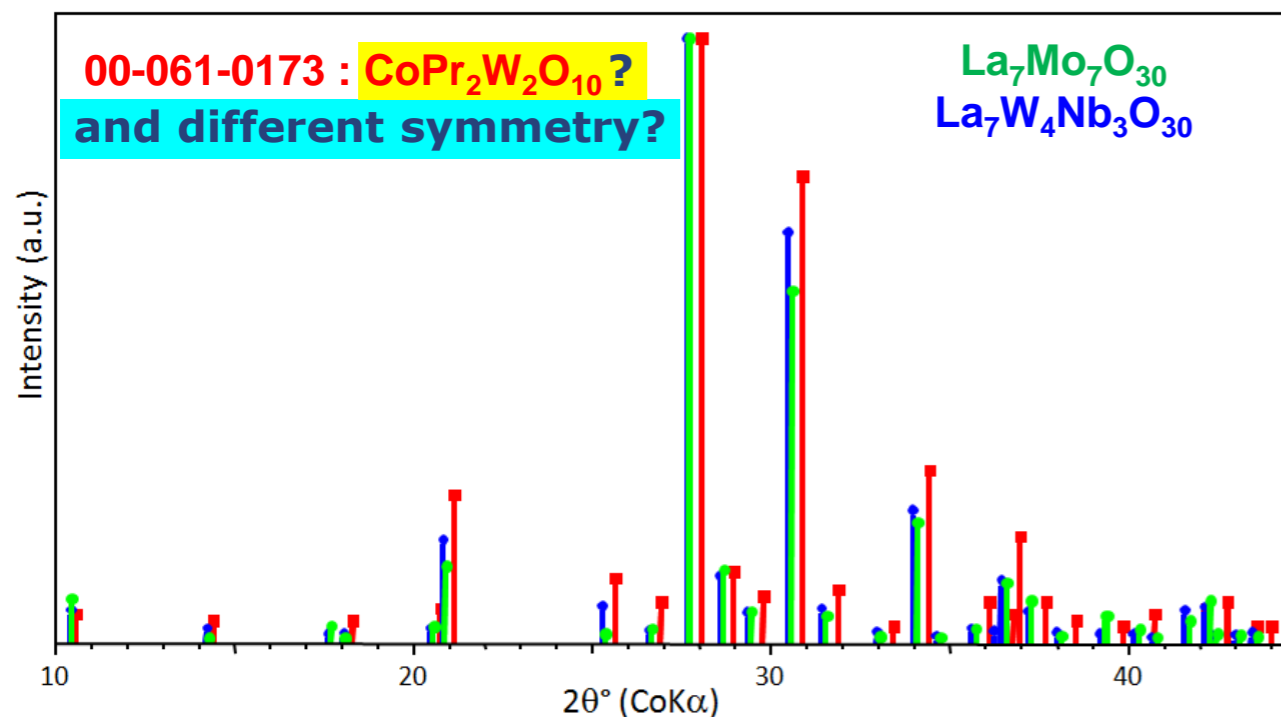
## NEW PRASEODYMIUM(III) AND *d*-ELECTRON METALS TUNGSTATES OF THE FORMULA $MPr_2W_2O_{10}$ ( $M=Mn, Co, Cd$ )

*E. Tomaszewicz\**

Department of Inorganic and Analytical Chemistry, Szczecin University of Technology, Al. Piastów 42, 71-065 Szczecin, Poland  
Three new compounds  $MPr_2W_2O_{10}$  ( $M=Mn, Co, Cd$ ) were prepared by the solid-state reaction. They are isostructural and crystallize in the orthorhombic system.  $MPr_2W_2O_{10}$  ( $M=Mn$  or  $Co$ ) melt incongruently above  $1150^\circ C$  and the solid product of melting is  $Pr_2W_2O_9$ . The  $CdPr_2W_2O_9$  compound starts decomposing in the solid-state at  $1156^\circ C$  to  $Pr_2W_2O_9$  and  $CdO$ .

- looking for new members with other rare earths:

Similar XRD patterns with different stoichiometry...



and interesting properties...

*Philosophical Magazine*

Vol. 92, No. 33, 21 November 2012, 4167–4181

### Dielectric and magnetic permittivities of three new ceramic tungstates $MPr_2W_2O_{10}$ ( $M = Cd, Co, Mn$ )

Z. Kukuła<sup>a</sup>, E. Tomaszewicz<sup>b</sup>, S. Mazur<sup>c</sup>, T. Groń<sup>a\*</sup>, H. Duda<sup>a</sup>, S. Pawlus<sup>a</sup>, S.M. Kaczmarek<sup>d</sup>, H. Fuks<sup>d</sup> and T. Mydlarz<sup>e</sup>

<sup>a</sup>University of Silesia, Institute of Physics, Katowice, Poland;

<sup>b,d</sup>West Pomeranian University of Technology, Szczecin, Poland;

<sup>c</sup>The Henryk Niewodniczański Institute of Nuclear Physics, Kraków, Poland;

<sup>e</sup>International Laboratory of High Magnetic Fields and Low Temperatures, Wrocław, Poland

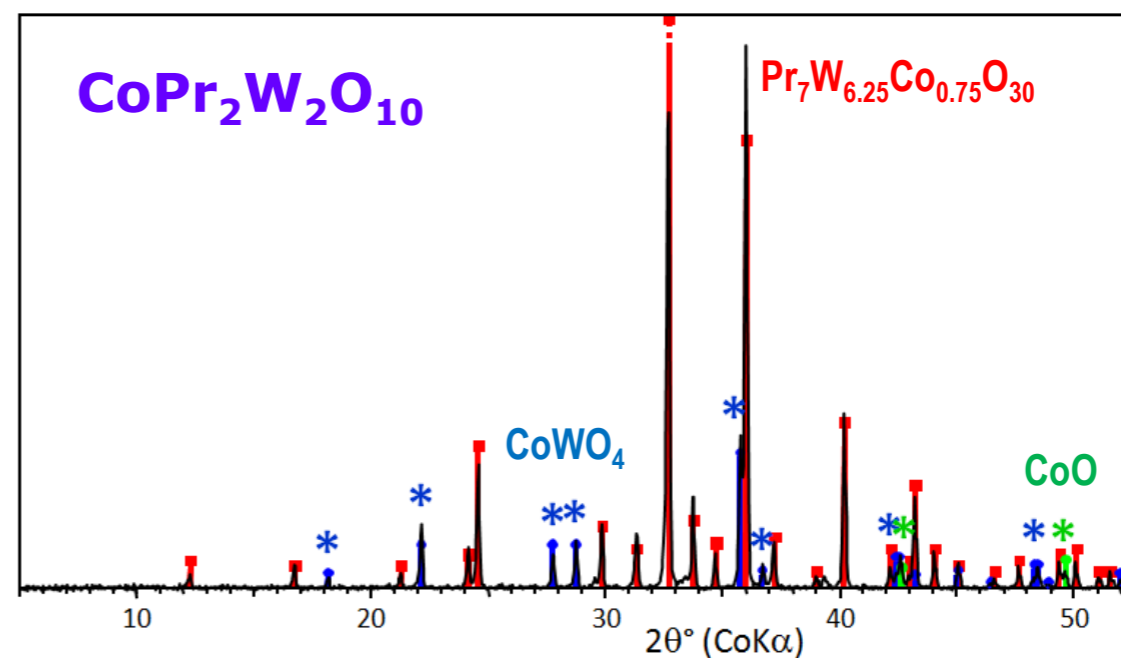
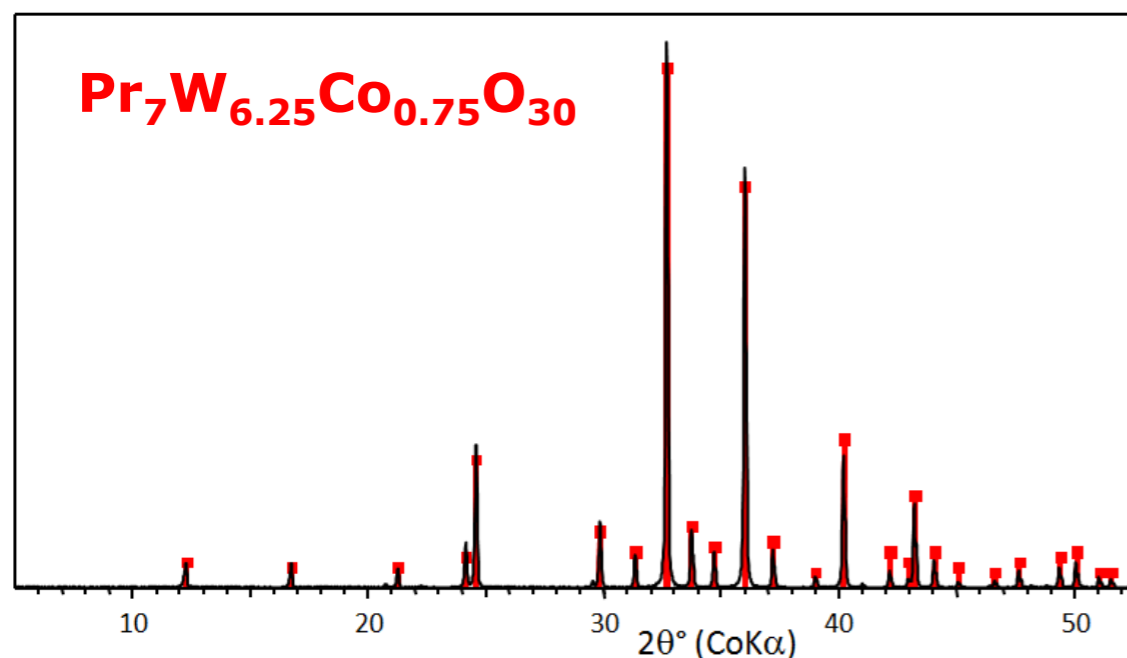
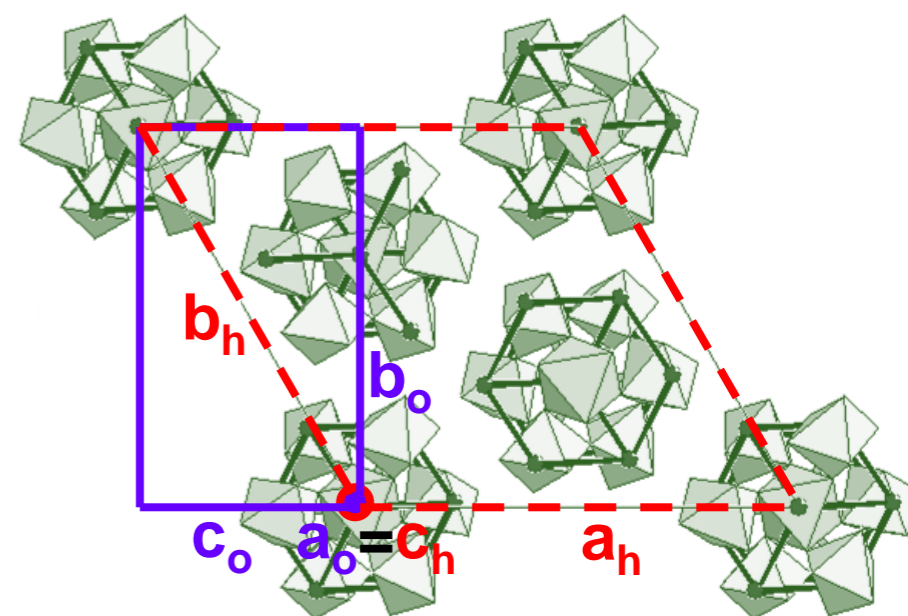
Broadband dielectric spectroscopy measurements revealed an anomalously large relative permittivity value ( $\epsilon_r = 884$ ) for  $MnPr_2W_2O_{10}$ , a smaller value ( $\epsilon_r = 156$ ) for  $CoPr_2W_2O_{10}$  and the smallest value ( $\epsilon_r = 22$ ) for  $CdPr_2W_2O_{10}$  at low frequency ( $\nu = 0.1$  Hz) and above room temperature in the insulating and paramagnetic state. Below 273 K, the relative permittivity ( $\epsilon_r \sim 24$ ) did not depend significantly on frequency for all the tungstates under study. Electrical resistivity, thermoelectric power, electron paramagnetic resonance, magnetic susceptibility and magnetization provided experimental evidence that the studied tungstates were paramagnetic insulators with low *n*-type conduction. Only in the case of  $MnPr_2W_2O_{10}$  was a ferrimagnetic order below 45 K observed. These effects are discussed within the framework of Maxwell–Wagner polarization, chemical covalent bonds and porosity mechanism.

# Other members of the $A_7B_7O_{30}$ family: the $MPr_2W_2O_{10}$ case

3)

- $MPr_2W_2O_{10}$  (M= Cd, Mn, Co, Tomaszewicz et al., from  $Pr_2WO_6 + MWO_4$ , ortho.  $a_0, b_0, c_0$ )
- $Pr_7W_{6.25}M_{0.75}O_{30}$  (M=Co, Zn, Lacorre, from elementary oxides, hexagonal  $a_h, c_h$ )

$M^{2+}$	$a_0$ or $c_h$ (Å)	$2 \cdot c_0$ or $a_h$ (Å)	$\sqrt{(b_0^2 + c_0^2)}$ or $b_h$ (Å)	$c_h/a_h$	$c_h/b_h$
Cd	6.8567	16.820	16.837	0.4077	0.4072
Mn	6.8076	16.819	16.832	0.4048	0.4044
Co	6.8021	16.817	16.822	0.4045	0.4044
Co	6.8094	16.8382	16.8382	0.4044	0.4044
Zn	6.8112	16.8428	16.8428	0.4044	0.4044



# Thank you for your attention !