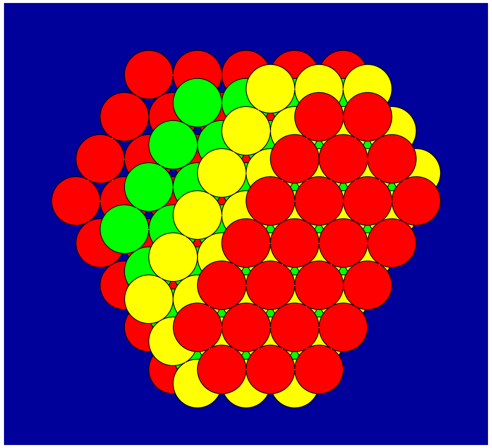
MODULAR ASPECTS IN INORGANIC STRUCTURES

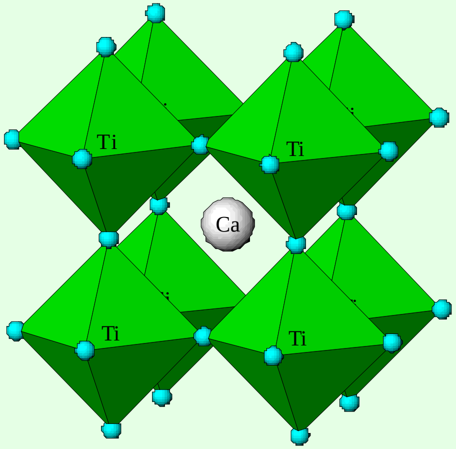
Giovanni FERRARIS

giovanni.ferraris@unito.it

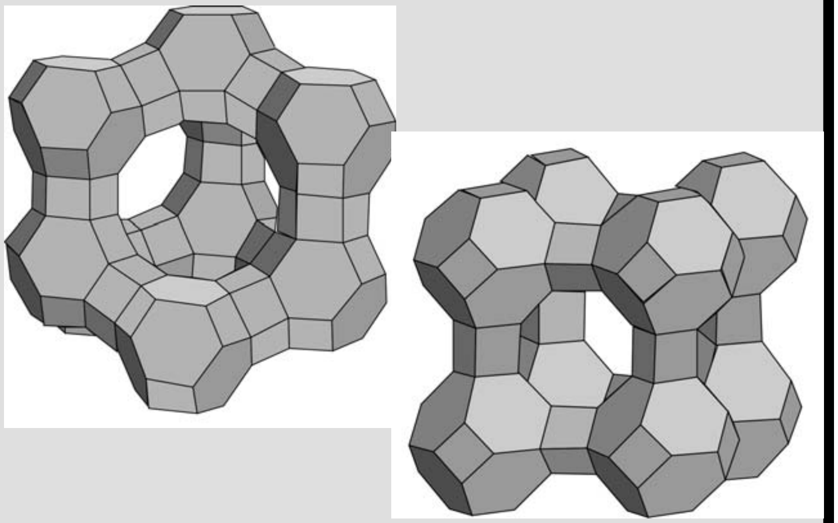
CRYSTAL STRUCTURES



Atoms

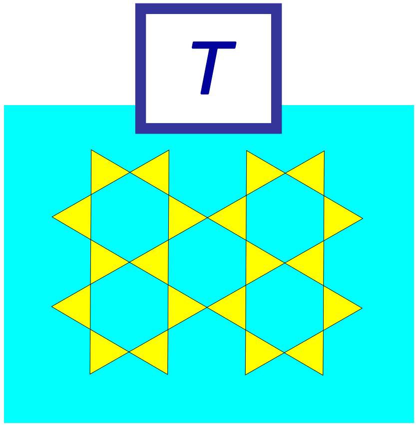


Coordination polyhedra



Cages of zeolites

TETRAHEDRAL / OCTAHEDRAL MODULES



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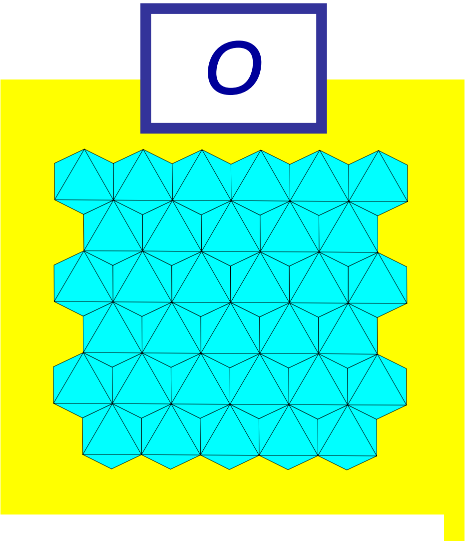

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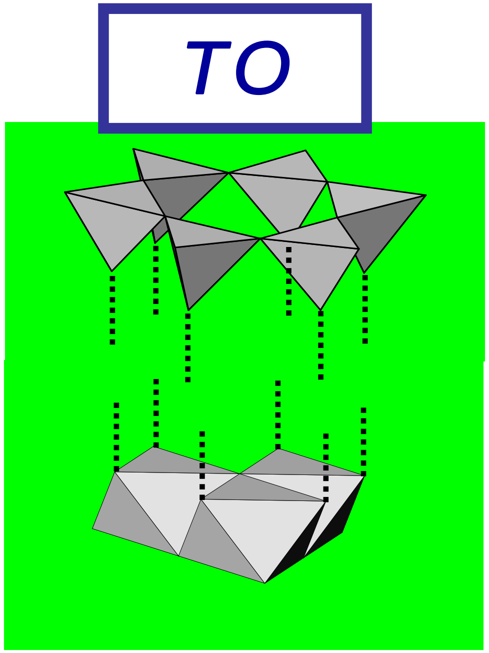
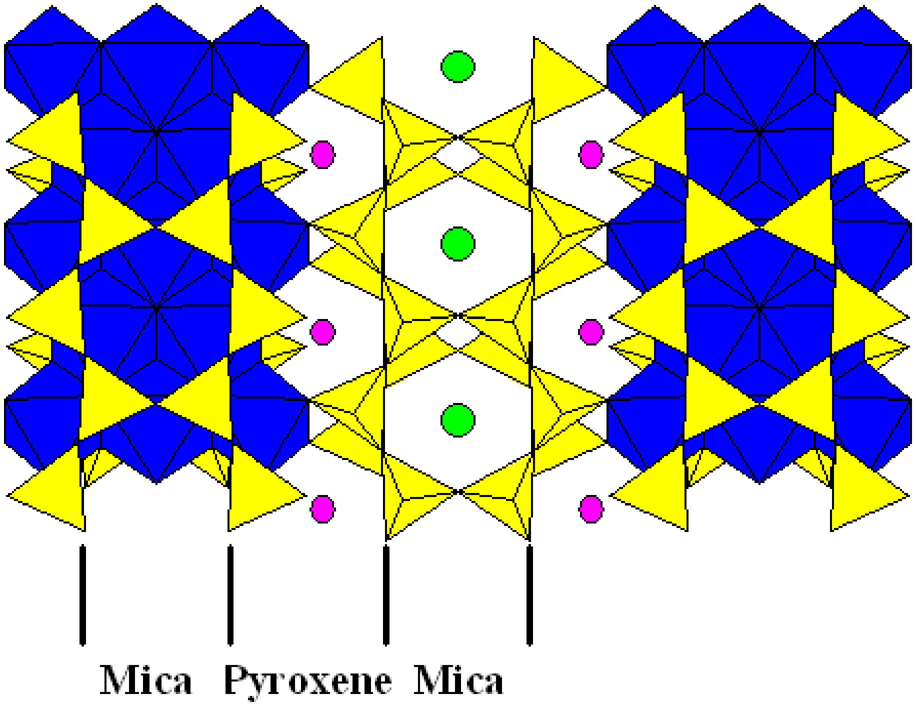
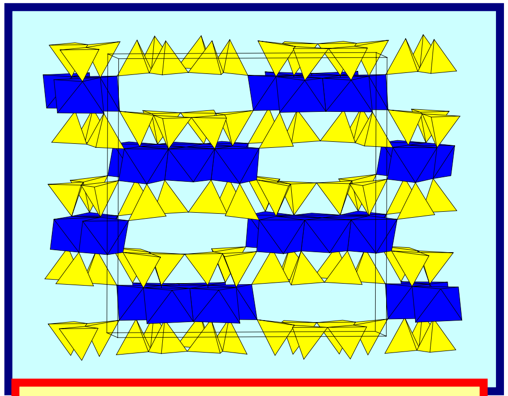




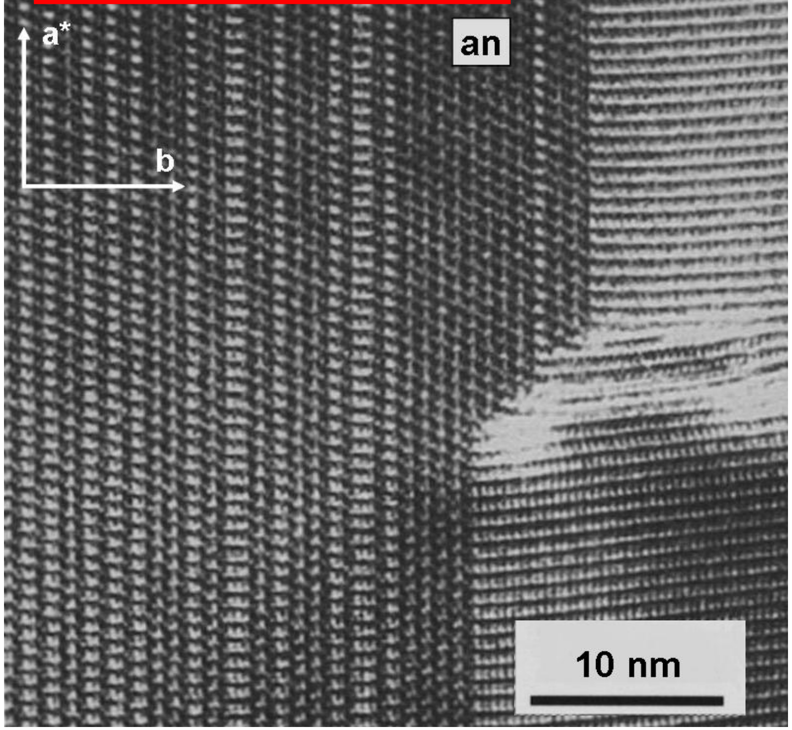
***TOT* beams →**

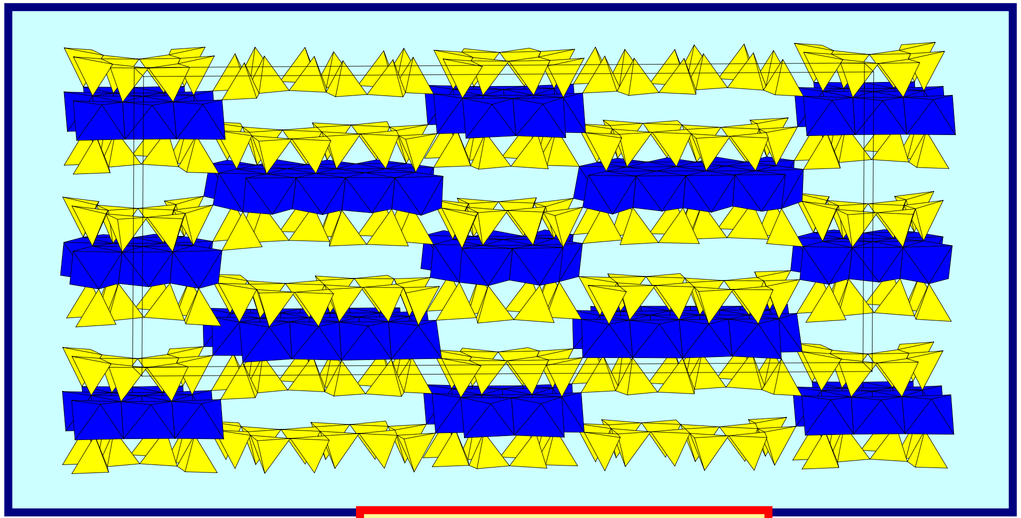
biopyriboles

BIOPYRIBOLES

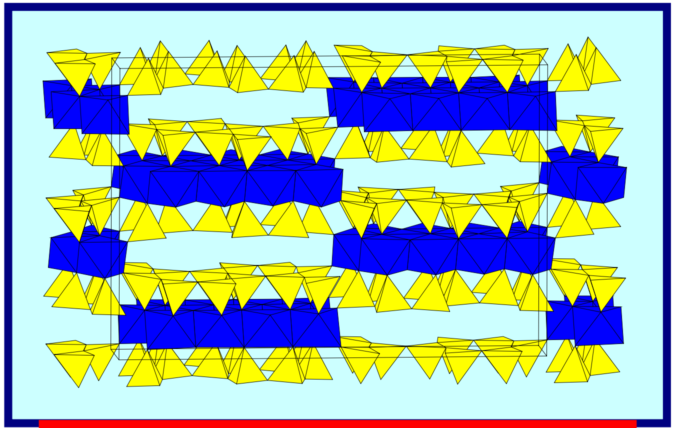


amphibole



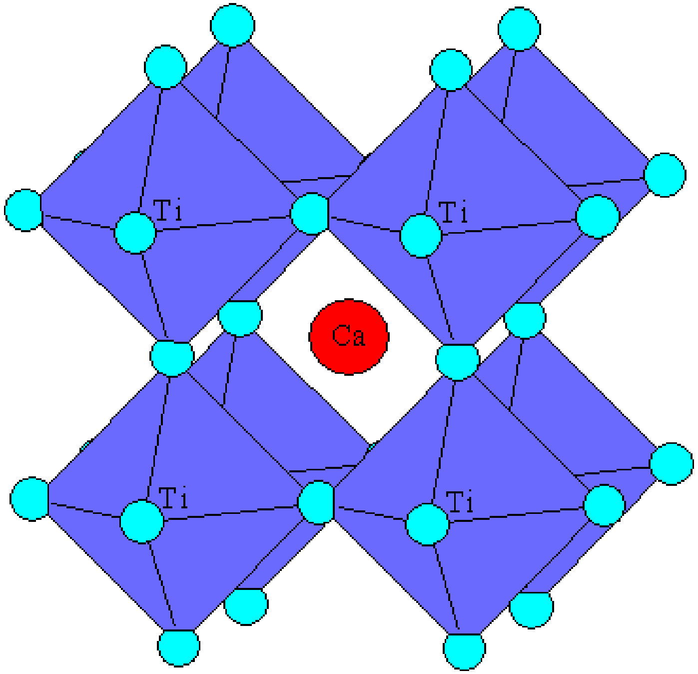


chesterite

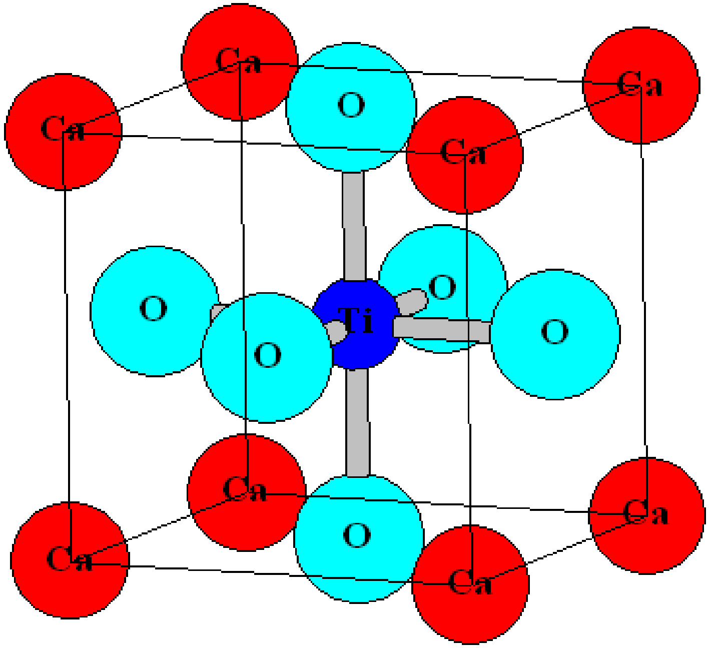


jimthompsonite

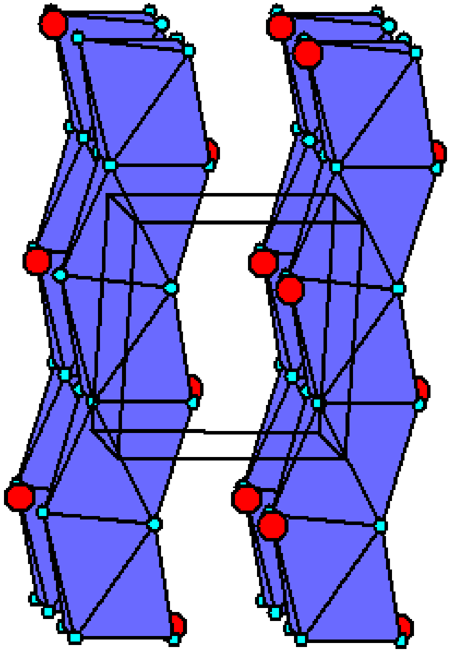
Cubic and Hexagonal perovskites



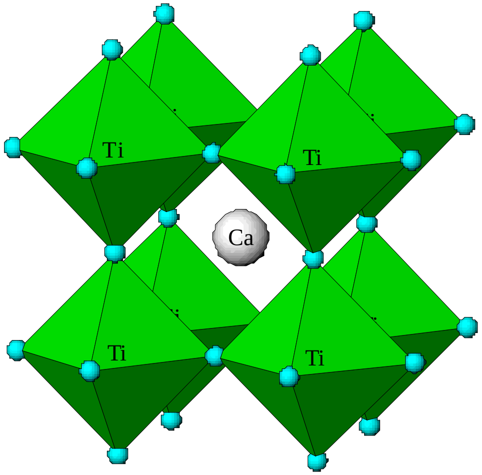
Cubic *ABC*
Polytype 3*C*



Hexagonal *AC*
Polytype 2*H*



PEROVSKITE MODULES AND TECHNOLOGY

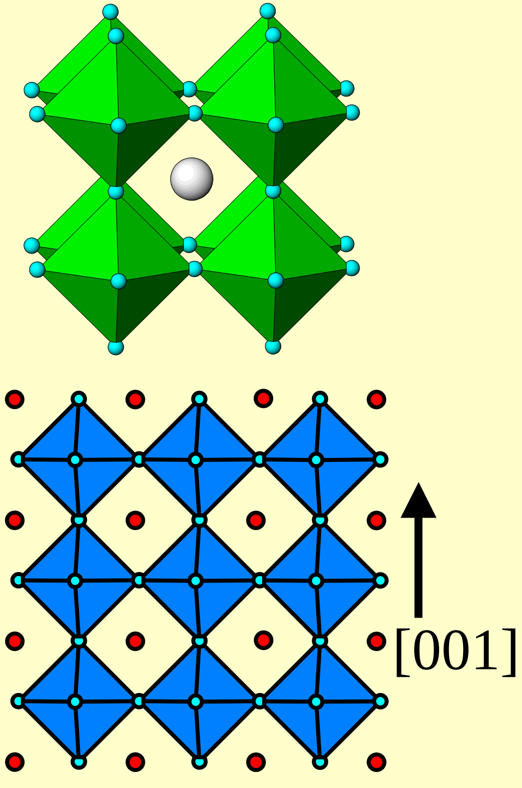


Modules of perovskite-type structure alternated with other modules occur in materials of interest for science and technology → hybrid or intergrowth perovskites

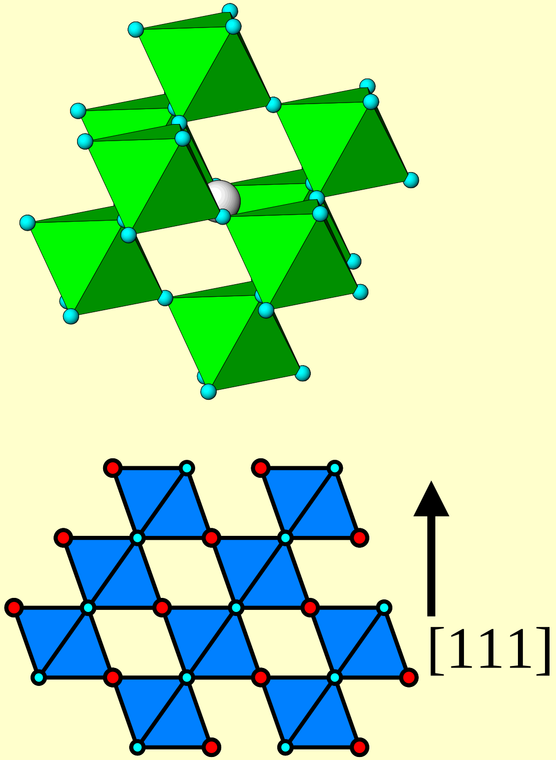
- **Three-dimensional** (sharing of corners along three directions)
- **Two-dimensional** (sharing of corners along two directions)
- **Mono-dimensional** (sharing of corners along one direction)
- **Zero-dimensional** (isolated octahedra)

PEROVSKITE MODULES AND TECHNOLOGY

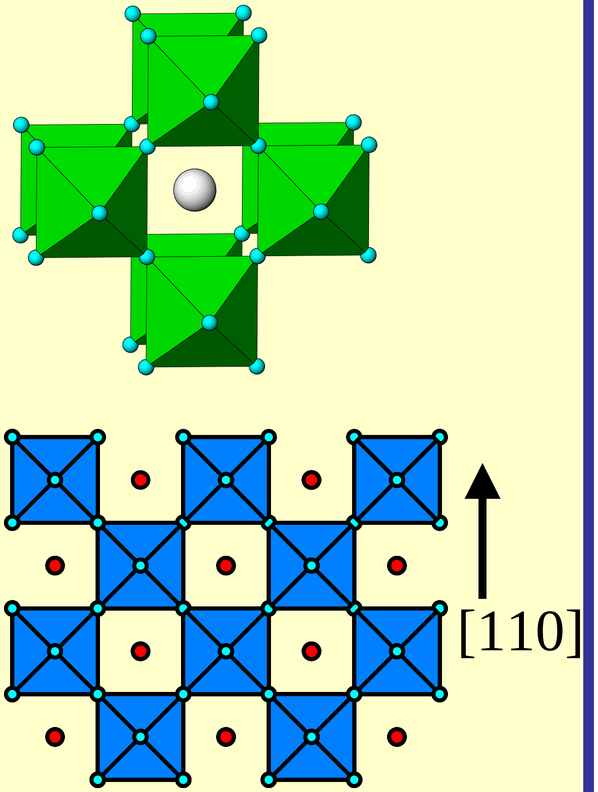
Projection in the planes (100), (1-10) and (001), in the order, of the octahedral sheets stacked along [001], [111], and [110]. Different periodicities in the stacked planes are selective of the interlayer.



(100)



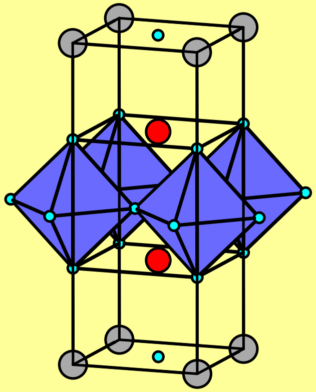
(1-10)



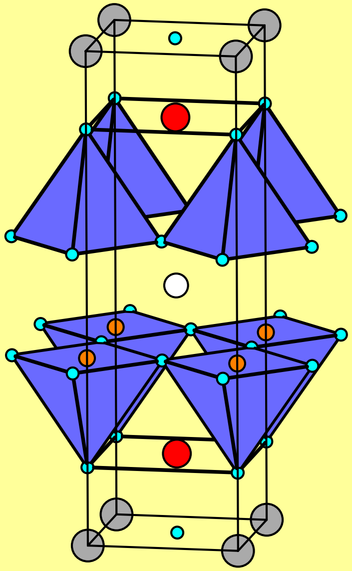
(001)

PEROVSKITE MODULES AND TECHNOLOGY

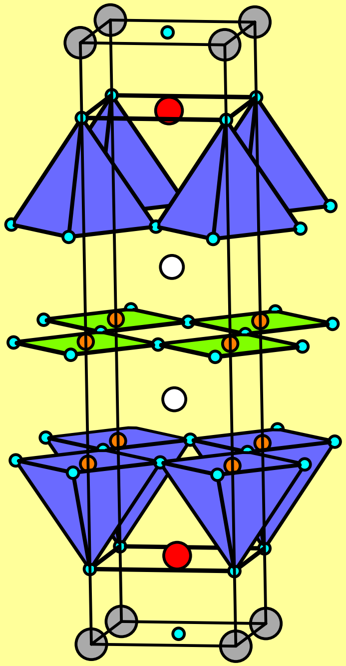
$TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ tallium cuprate series of superconductors



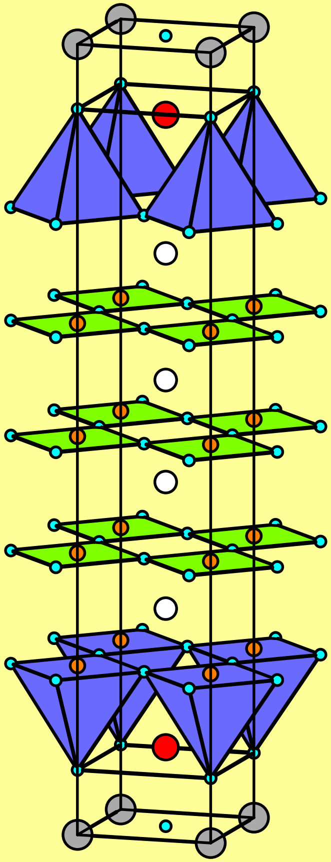
n = 1
121



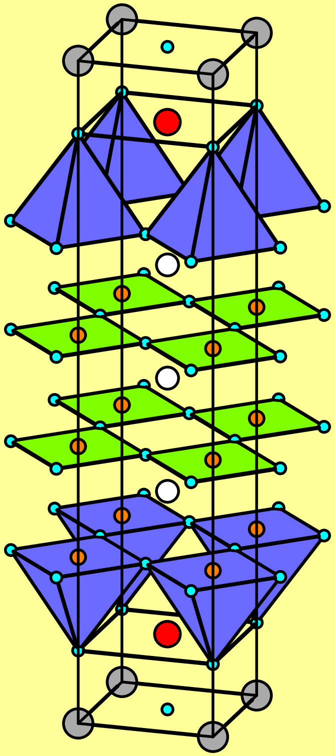
n = 2
1212



n = 3
1223



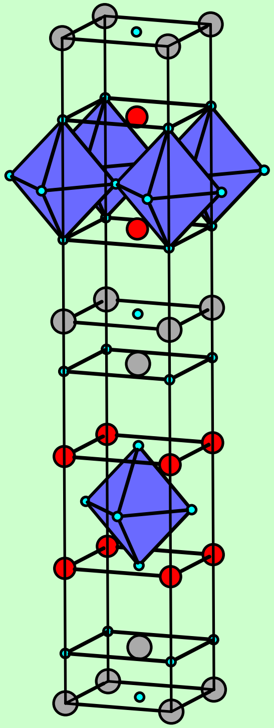
n = 4
1234



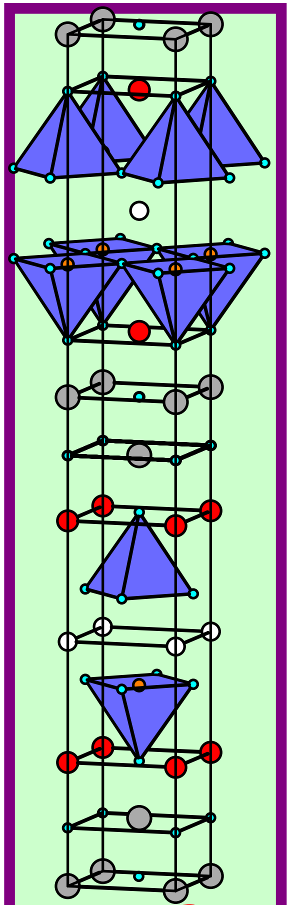
n = 5
1245

PEROVSKITE MODULES AND TECHNOLOGY

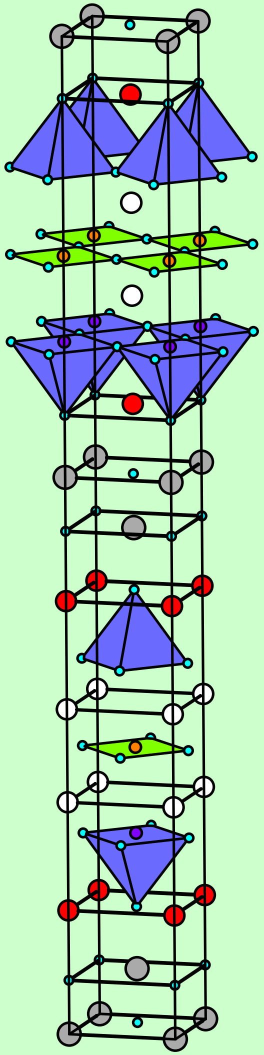
$Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ tallium cuprate series of superconductors



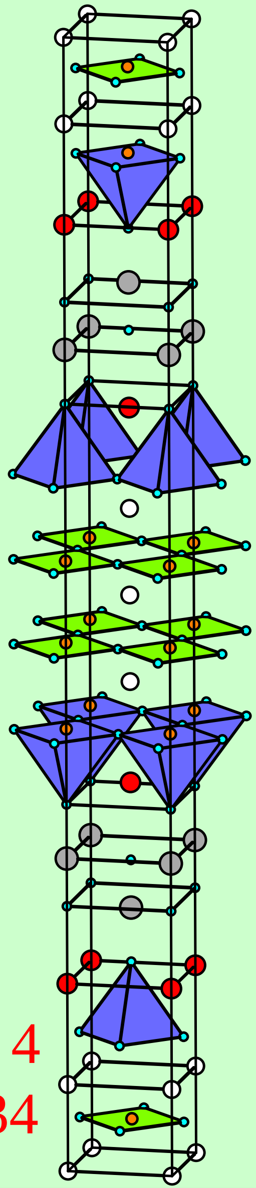
n = 1
221



n = 2
2212



n = 3
2223

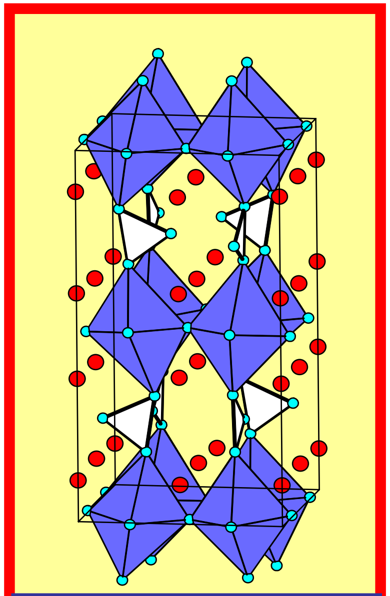


n = 4
2234

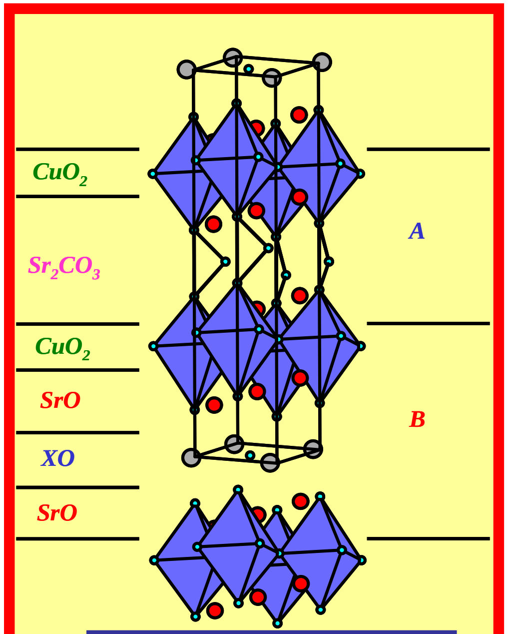
PEROVSKITE MODULES AND TECHNOLOGY

SUPERCONDUCTING OXYCARBONATES

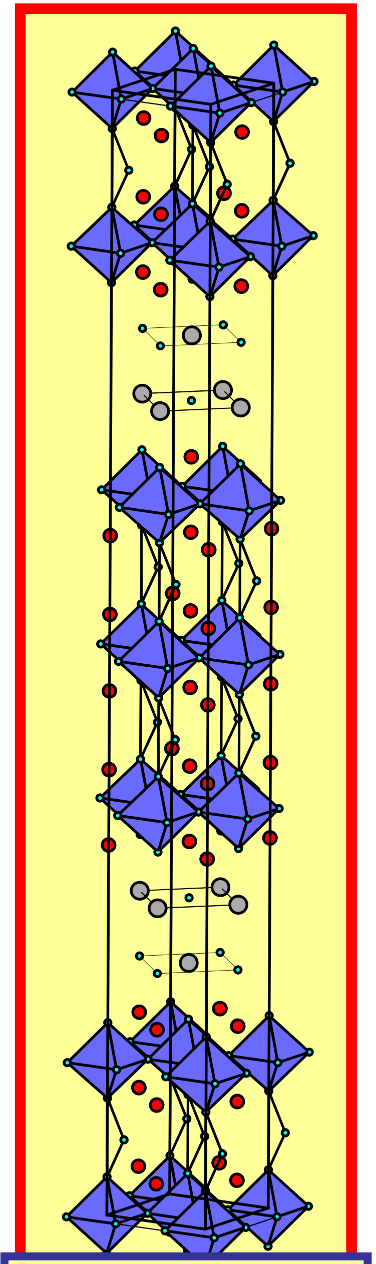
Polysomatic series $(Sr_2CuO_2CO_3)_m(X_pSr_2CuO_5)_n$ ($m > n$) based on (001) perovskite layers connected by CO_3 groups



$m = 1$ $n = 0$



$m = 1$ $n = 1$



$m = 2$ $n = 1$

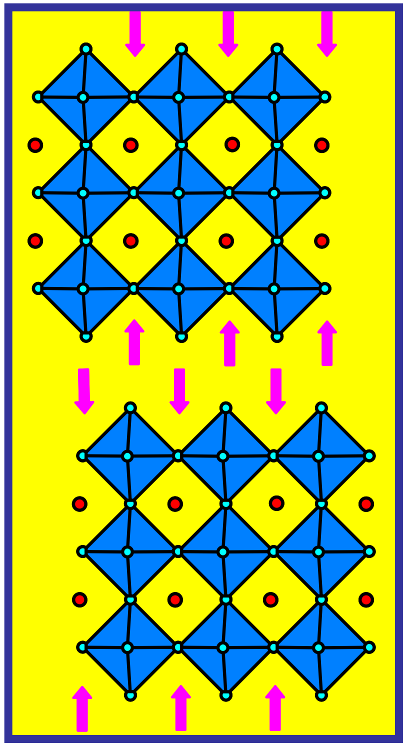
PEROVSKITE MODULES AND TECHNOLOGY
ORGANIC-INORGANIC HYBRID PEROVSKITES

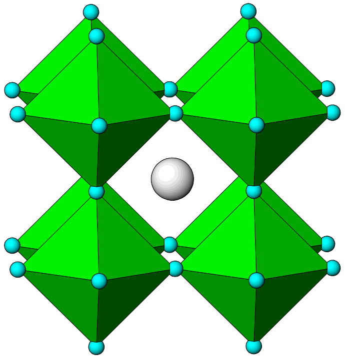
$(RNH_3)_2A_{n-1}B_nX_{3n+1}$ series based on (001) layers

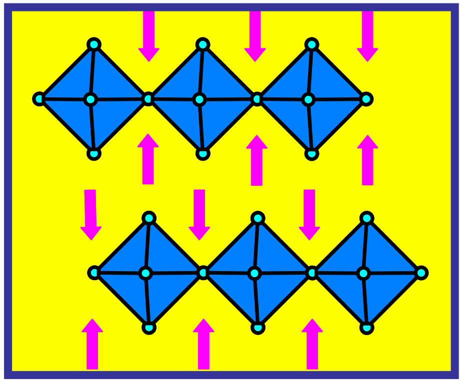
Engineering in the **$(C_4H_9NH_3)_2(CH_3NH_3)_{n-1}Sn_nI_{3n+1}$ polysomatic series**

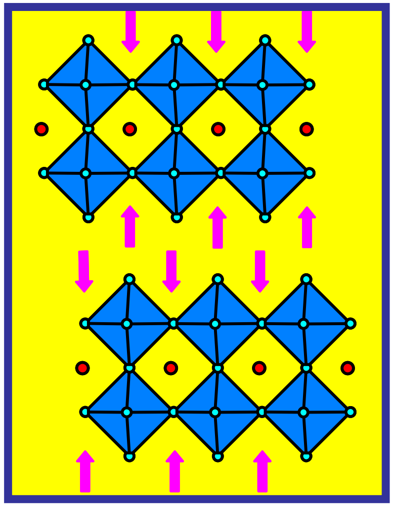
1. $n = 1$ → large band gap **semiconductor**
2. The resistivity decreases by increasing n
3. Metallic behaviour for $n \geq 3$
4. The $n = \infty$ material **$(CH_3NH_3)SnI$** is a p-type metal

Non-linear optical properties and **electroluminescence**

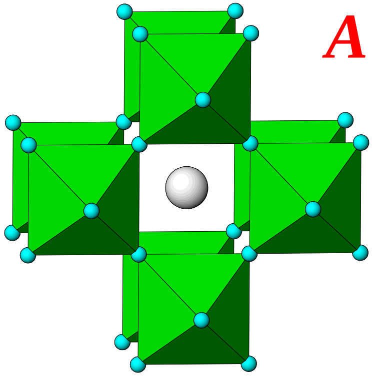




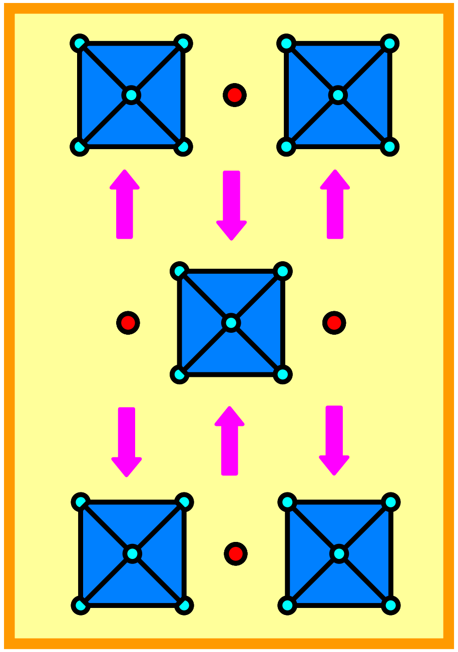


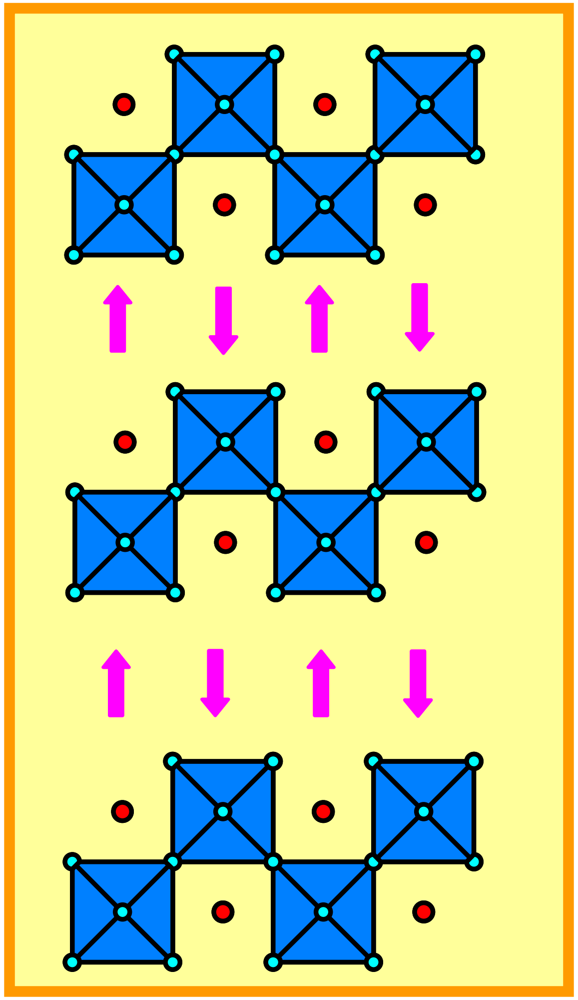


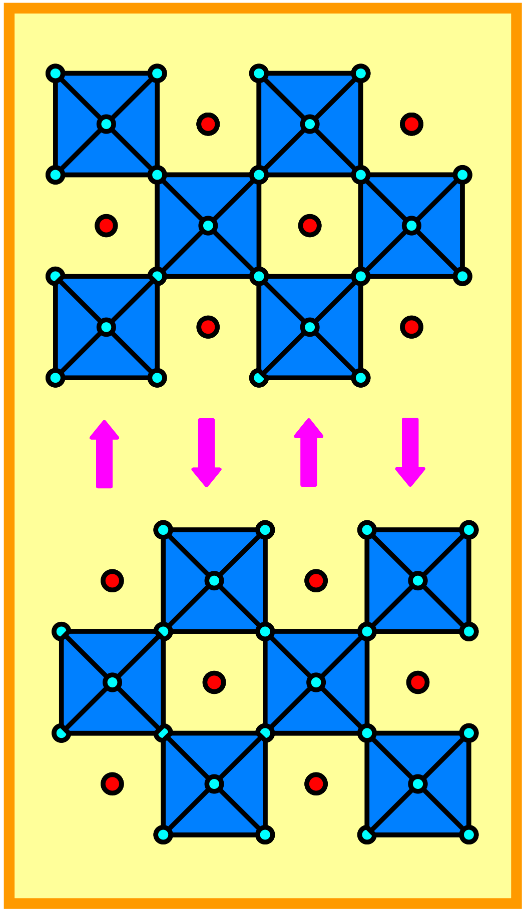
PEROVSKITE MODULES AND TECHNOLOGY
ORGANIC-INORGANIC HYBRID PEROVSKITES



$A'_2A_mB_mX_{3m+2}$ (*n* = 1, 2, 3) series based on (110) layers

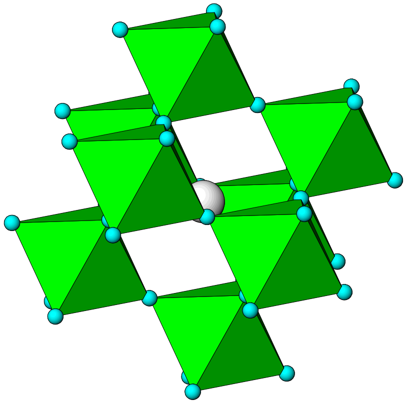


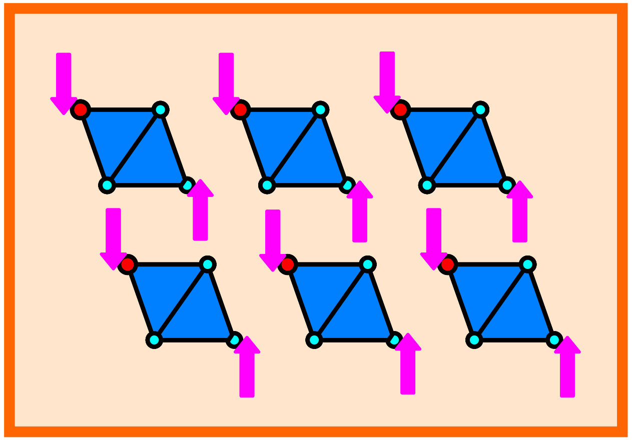


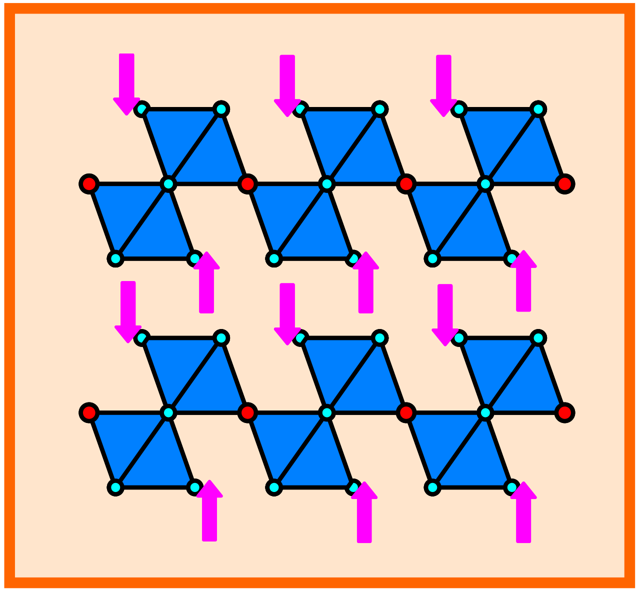


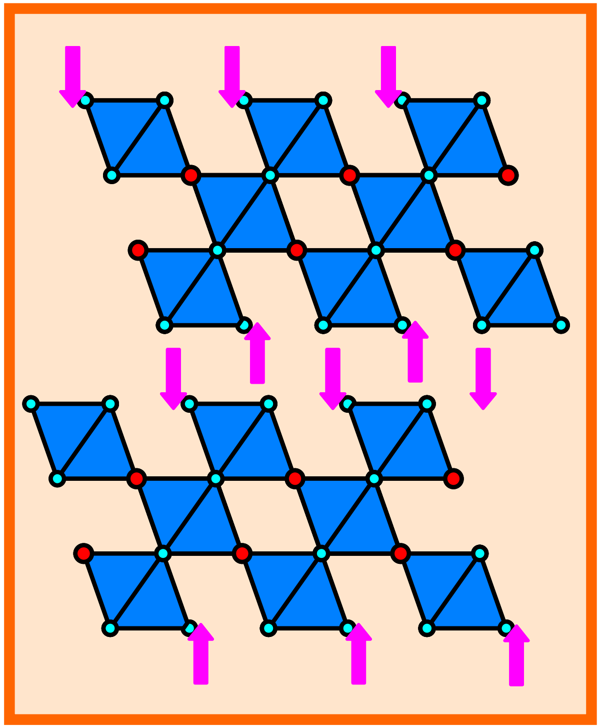
PEROVSKITE MODULES AND TECHNOLOGY
ORGANIC-INORGANIC HYBRID PEROVSKITES

$A'_2A_{q-1}B_qX_{3q+3}$ (*n* = 1, 2, 3) series based on (111) layers









PEROVSKITE MODULES AND TECHNOLOGY
ORGANIC-INORGANIC HYBRID PEROVSKITES

Perovskite modules (anion)
intercalated with organic molecules (cation).

Combining properties of the organic part (e.g., luminescence and plastic) with those of the inorganic part (e.g., electrical and mechanical).

Tailoring can play on:

- Nature of the *A* (dodecahedral) and *B* (octahedral) cations.
- Nature of the *X* anion (usually a halide).
- Orientation and thickness of the perovskite layer.

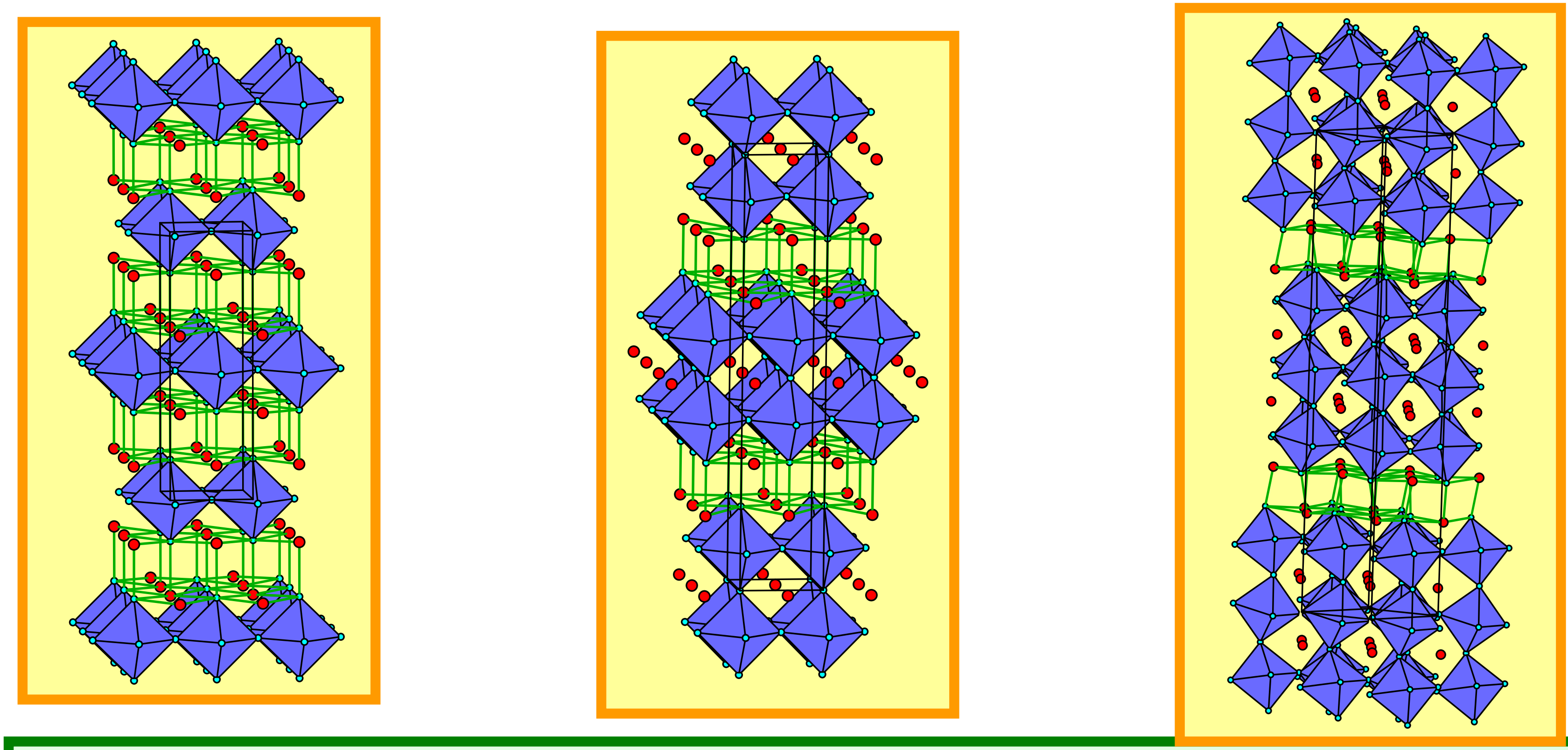
Series of organic-inorganic layered perovskites can be built by:

1. Keeping fix the perovskite layer and changing organic interlayer;
2. Keeping fix the interlayer and changing the thickness of perovskite;
3. Varying the thickness of both layers.

PEROVSKITE MODULES AND TECHNOLOGY

$A_{n+1}B_{n}X_{3n+1}$ polysomatic series (Ruddlesden-Popper series)

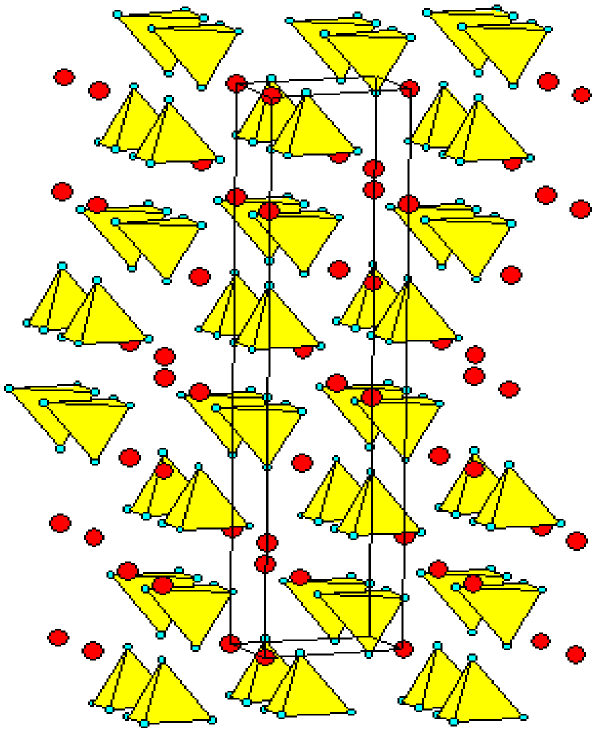
n **(001) perovskite layers alternate with one sodium-chloride-like layer**

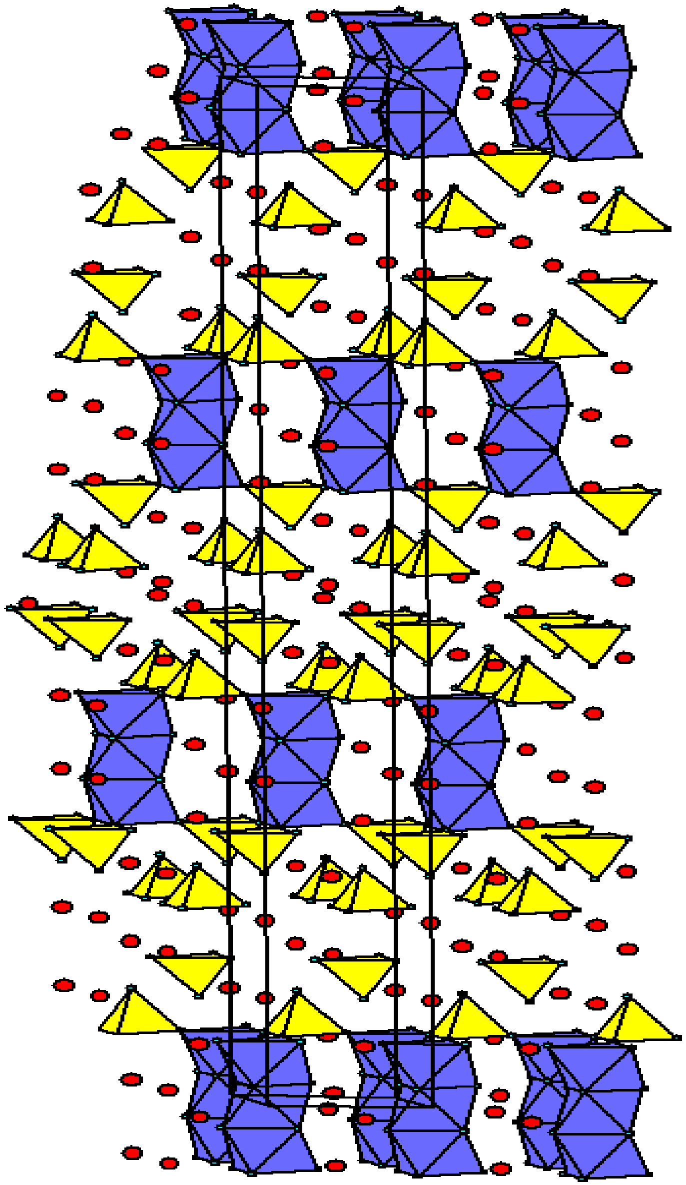


On $(La,Ba)_2CuO_4$ (*n* = 1) Bednorz and Müller (1986) discovered high-*Tc* superconductivity with *Tc* ~ 30 K.

$Sr_{1.8}La_{1.2}Mn_2O_7$ (*n* = 2) shows colossal magnetoresistance.

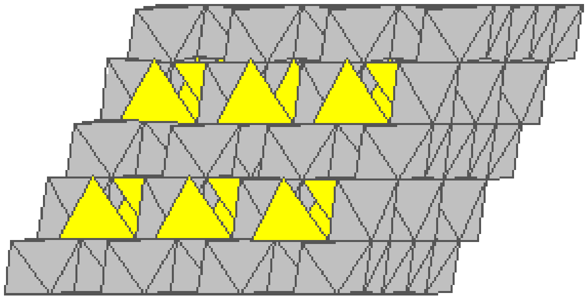
PALMIERITE TYPE



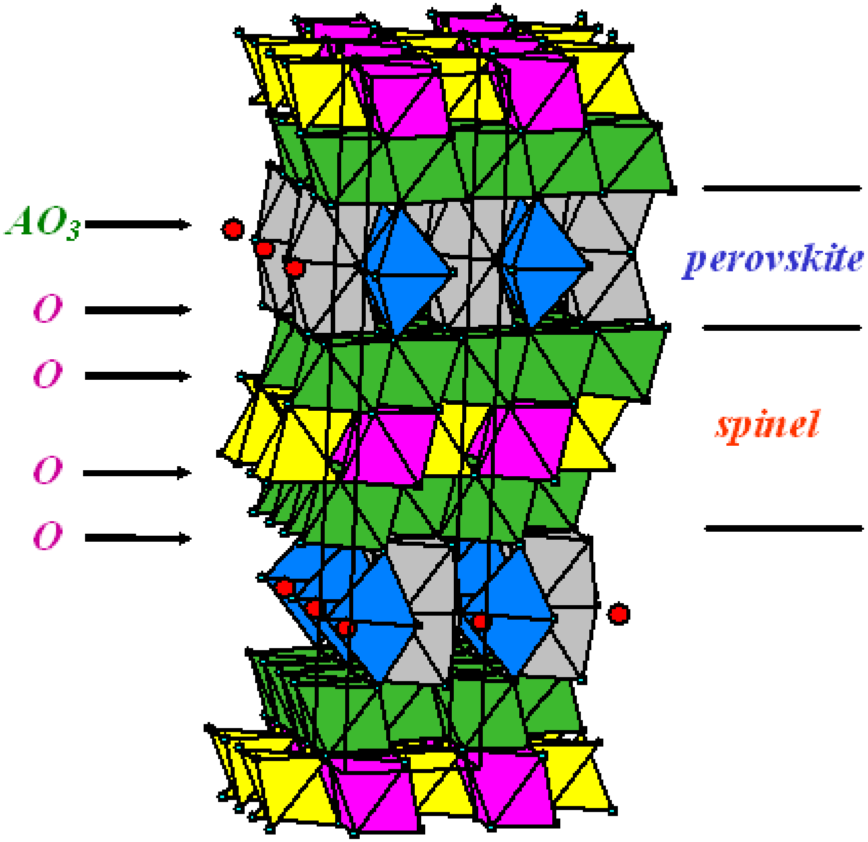


LEFT - Palmierite-type structure = 9R perovskite with partial filling of tetrahedral and octahedral sites.
RIGHT – Alternation of palmierite-type and 2H-perovskite modules

MAGNETOPLUMBITE-TYPE



(111) spinel layers

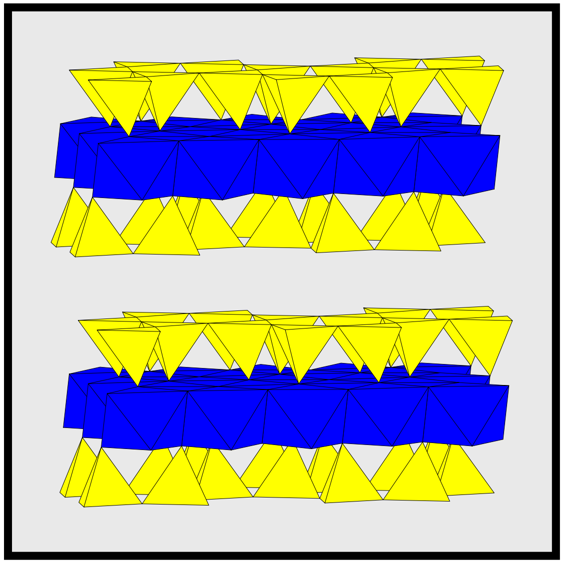


TETRAHEDRAL / OCTAHEDRAL MODULES
LAYER SILICATES

T+O+T

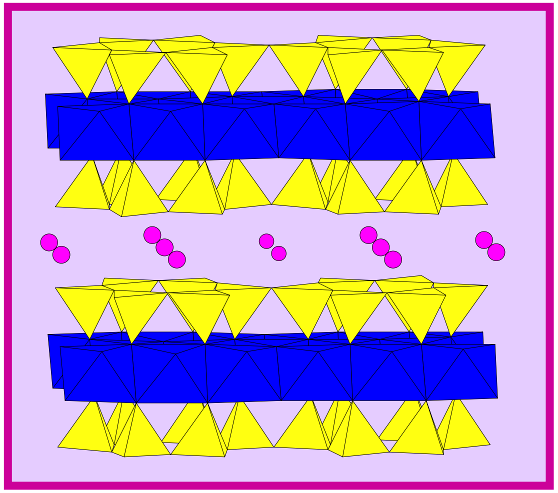
+ empty interlayer

talc



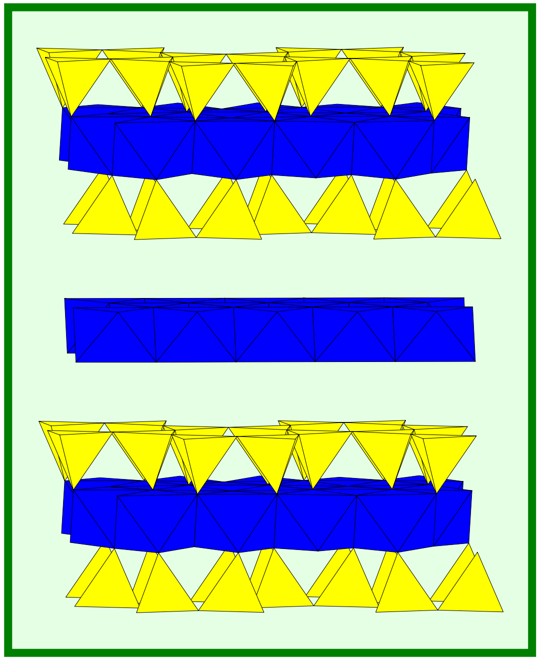
+ cations

mica



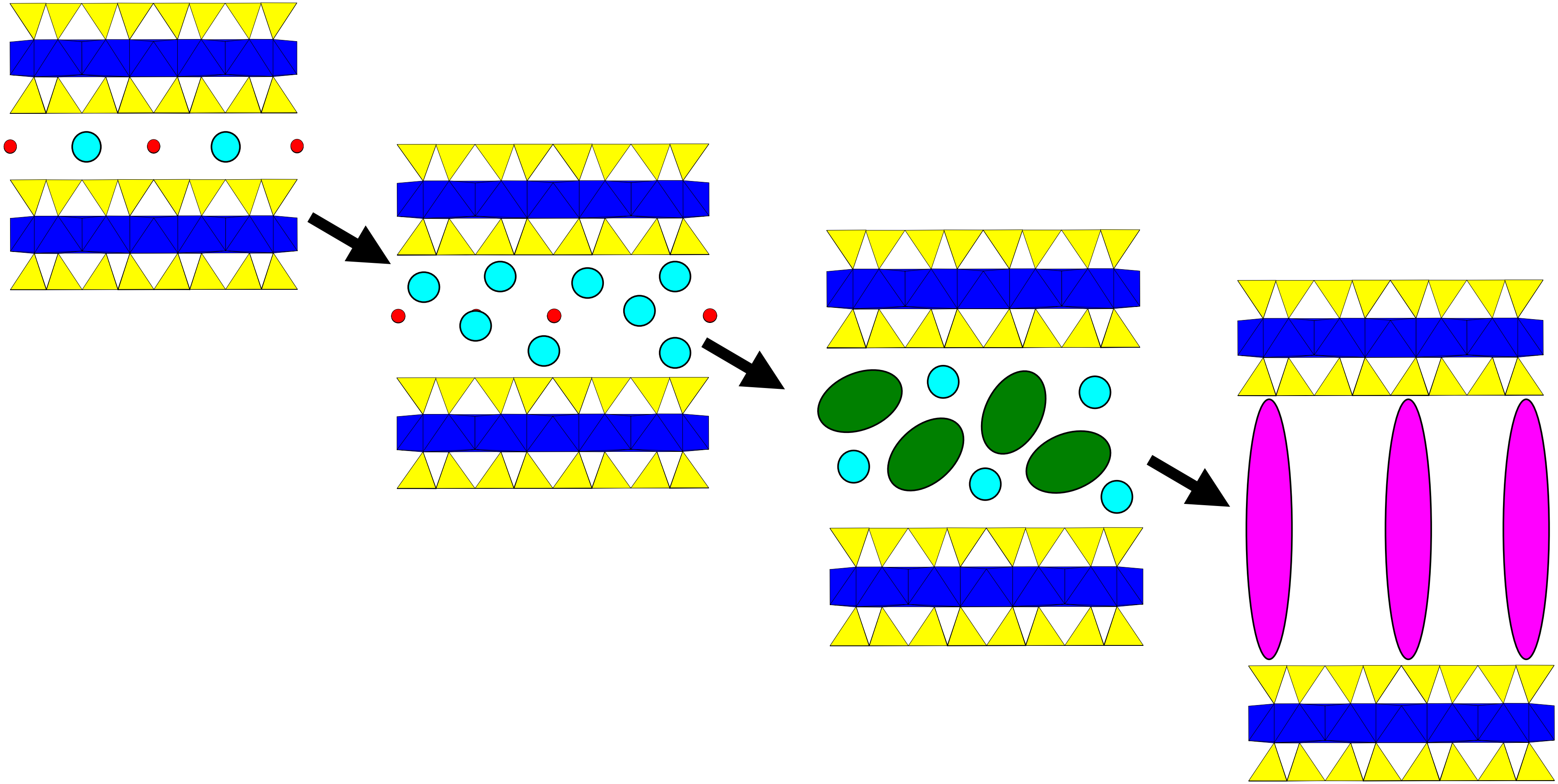
+ O layer

chlorite

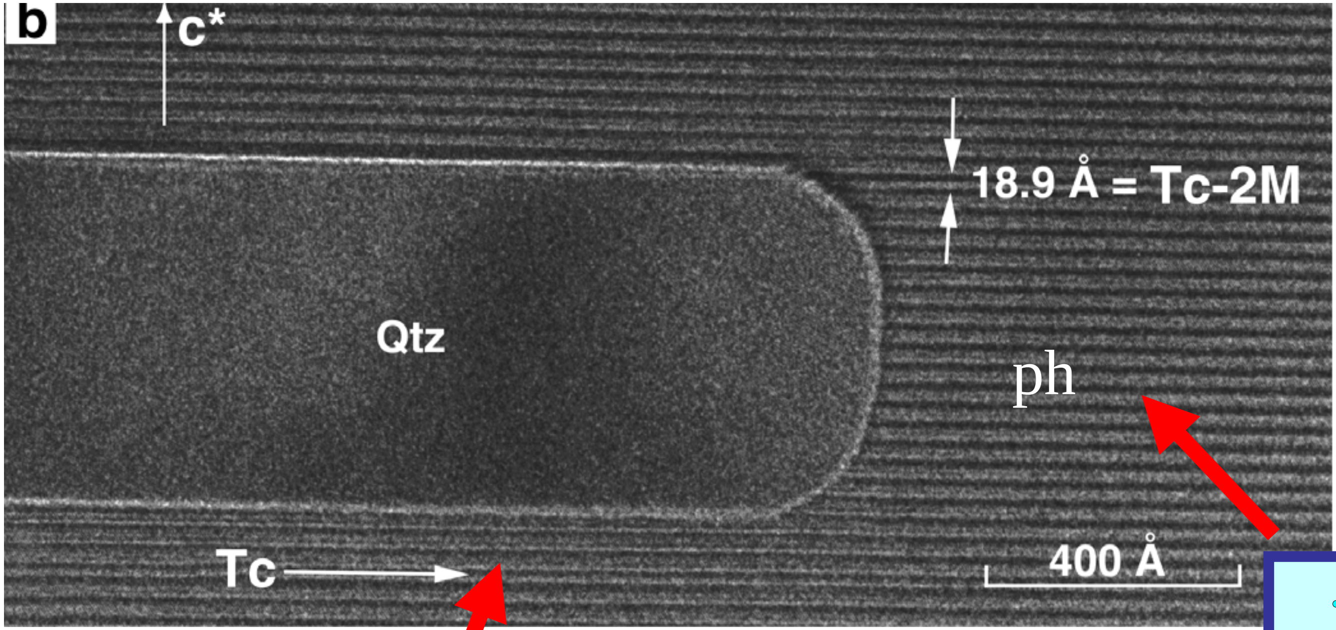


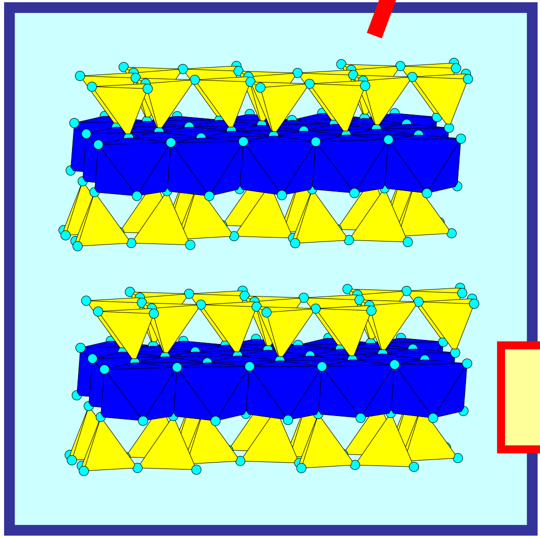
TOT MODULES AND TECHNOLOGY

PILLARED CLAYS



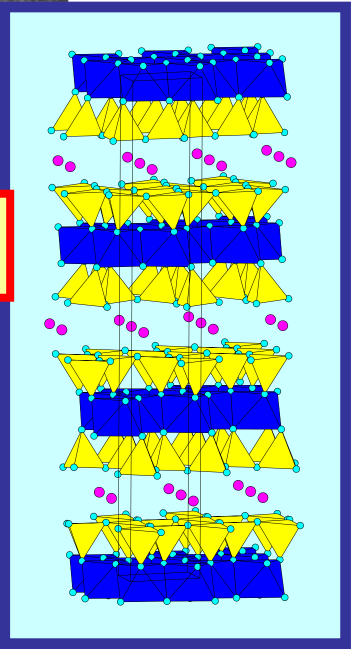
MODULES IN REAL STRUCTURES





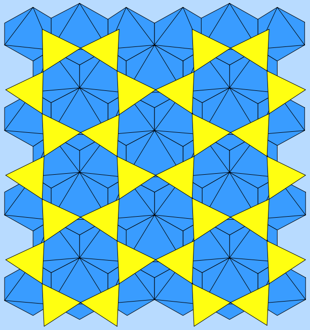
talc

phengite



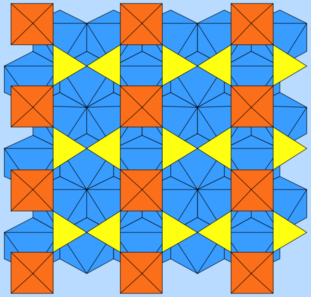
HETEROPHYLLOSILICATES

A row of Ti polyhedra periodically substitutes a row of Si tetrahedra in a *TOT* layer. Three types of *HOH* layers are known. B_mM_n polysomatic series.

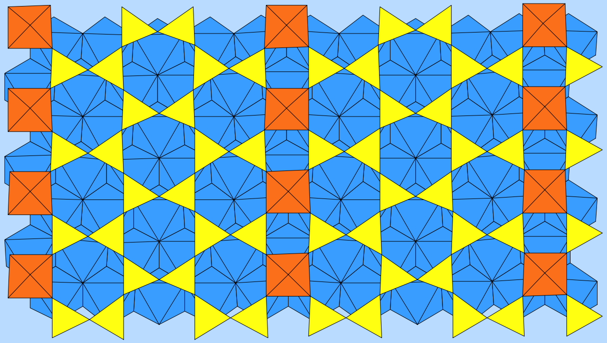


MICA (module *M*)

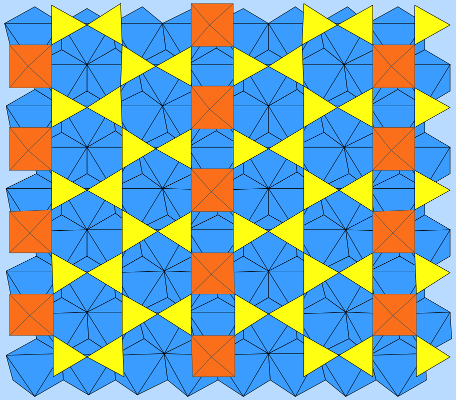
+ Ti octahedra (pyramids) =



BAFERTISITE (module *B*)



NAFERTISITE (*B_1M_2*)



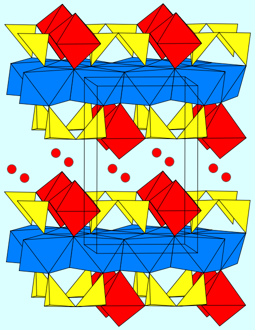
ASTROPHYLLITE (*B_1M_1*)

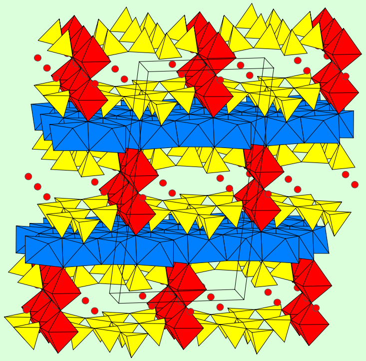
MEMBERS OF THE B_mM_n SERIES

$I_{2+n}Y_{4+3n}[\mathrm{Ti}_2(\mathrm{O})_{2+p}\mathrm{Si}_{4+4n}\mathrm{O}_{14+10n}](\mathrm{O})_{2+2n}$

B_1M_0 → bafertisite

$\mathrm{Ba_2\{(Fe,Mn)_4[Ti_2O_2(O,OH)_2Si_4O_{14}](O,OH)_2\}}$



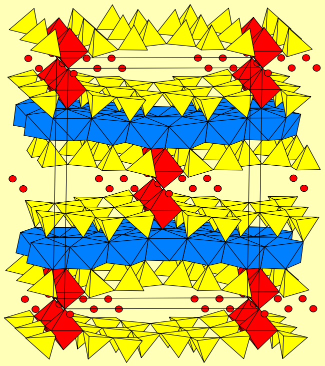


B_1M_1 → astrophyllite

$\mathrm{(K,Na)_3(Fe,Mn)_7[Ti_2O_3Si_8O_{24}](O,OH)_4}$

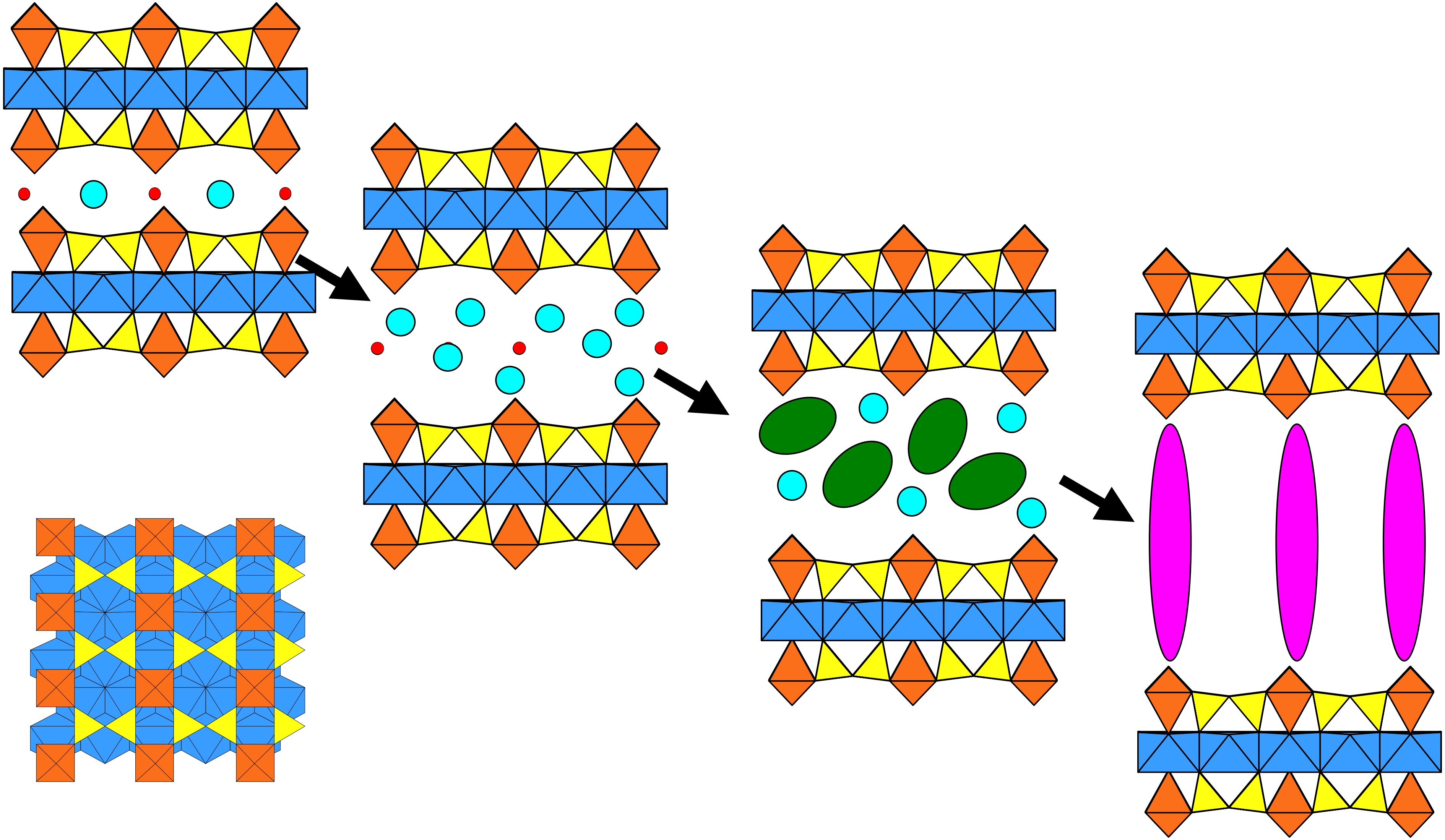
B_1M_2 → nafertisite

$\mathrm{(Na,K,\ \ )_4(Fe^{2+},Fe^{3+},\ \ )_{10}[Ti_2O_3Si_{12}O_{34}](O,OH)_6}$

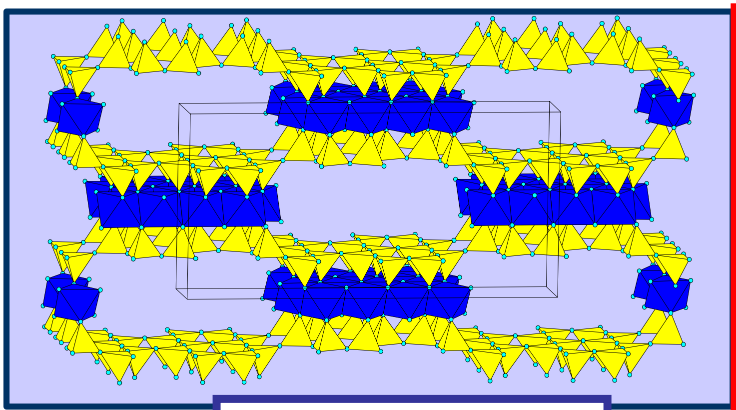


HOH MODULES AND TECHNOLOGY

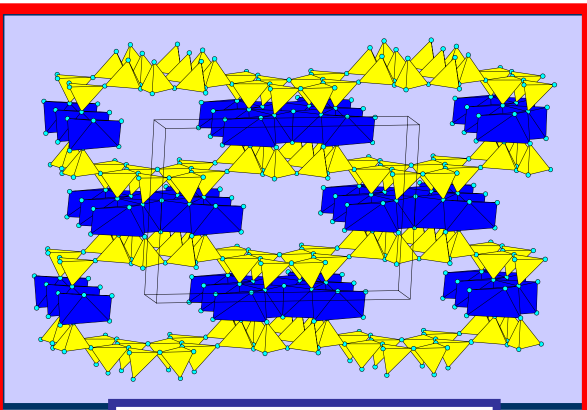
PILLARED HETEROPHYLLOSILICATES?



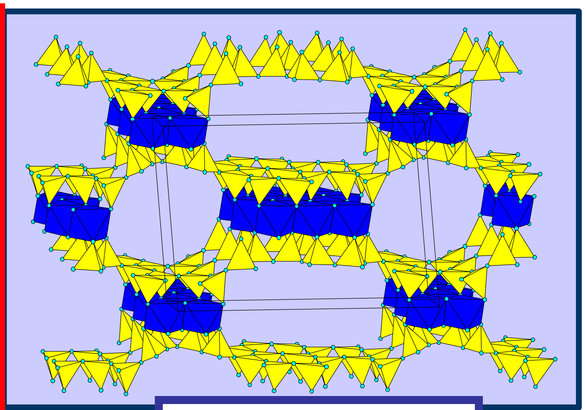
PALYSEPIOLES



sepiolite



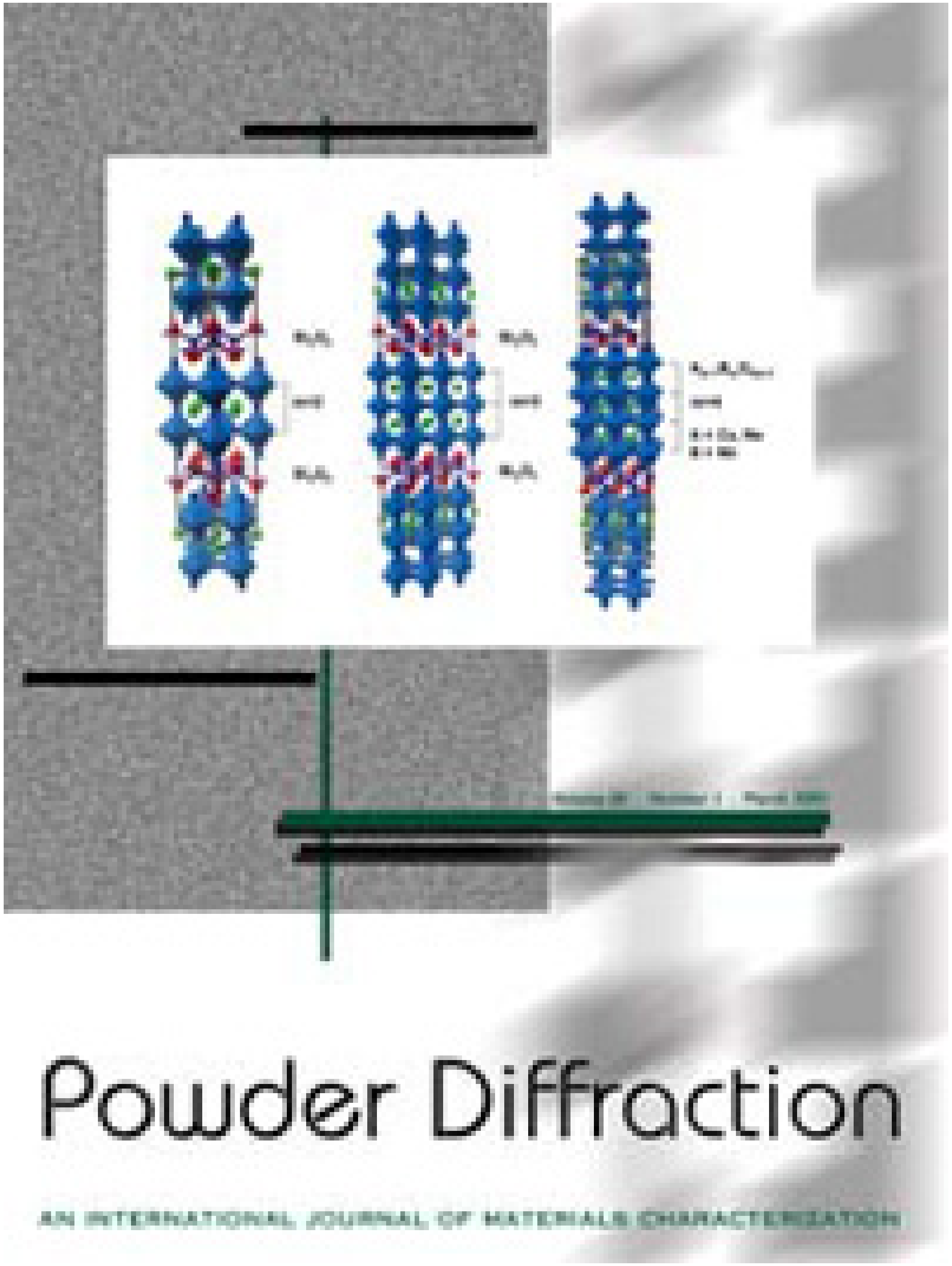
palygorskite



kalifersite

+

Indigofera suffruticosa



Powder Diffraction

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