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New phases in the good old manganites

or

Structural trends in oxygen-vacancy-ordered $La_xSr_{1-x}MnO_y$ perovskite manganites and the $A_{4+n}B_{4+n}O_{10+3n}$ homologous series.

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&

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A bit of personal history

- BSc (1995), MSc (1999) and PhD (2003) in Chemistry (Crystallography) at Universidad de la República (Uruguay State University) in Montevideo, Uruguay. Thesis Advisor: Prof. Alvaro W. Mombrú
- Assistant Proffessor of Crystallography (with tenure) since 2001, on paid leave.

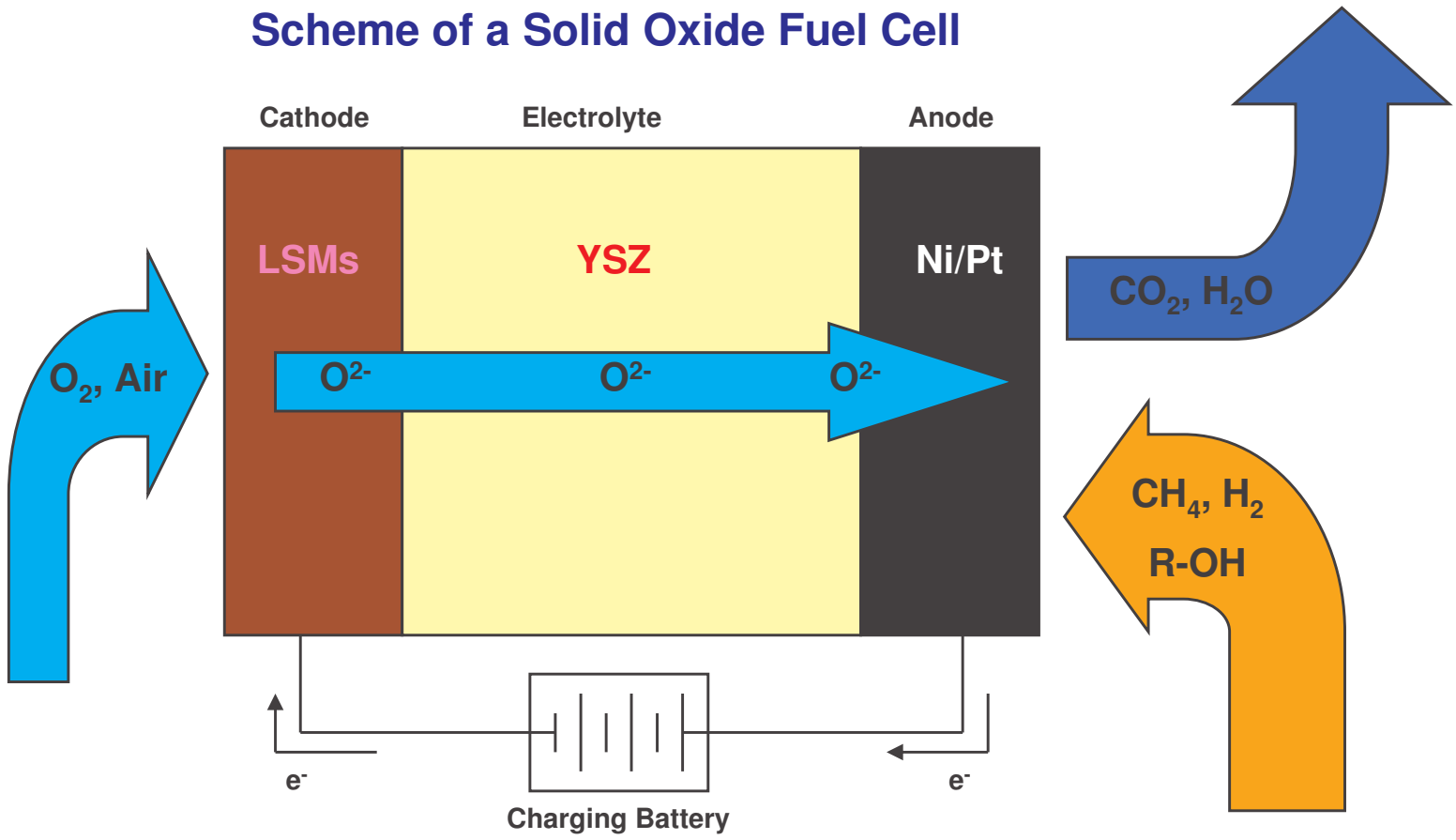
- Postdoctoral Appointee, Materials Science Division, Neutron and X-ray scattering Group.
  - Since April 29th, 2005
  - Leaving on April 28th

Overview

- Motivation: Perovskite materials for S.O.F.C. cathodes
- Experimental work and initial results: NPD experiments in the $La_xSr_{1-x}MnO_y$ system.
- Re-focusing: Oxygen-vacancy, charge and orbital ordering in $Sr_5Mn_5O_{13}$ and $Sr_7Mn_7O_{19}$
- A new homologous series $A_{4+n}B_{4+n}O_{10+3n}$ built upon BO_5 pyramids and BO_6 octahedra
- Conclusions, take home message.
- Perspectives

Solid Oxide Fuel Cell (SOFC):

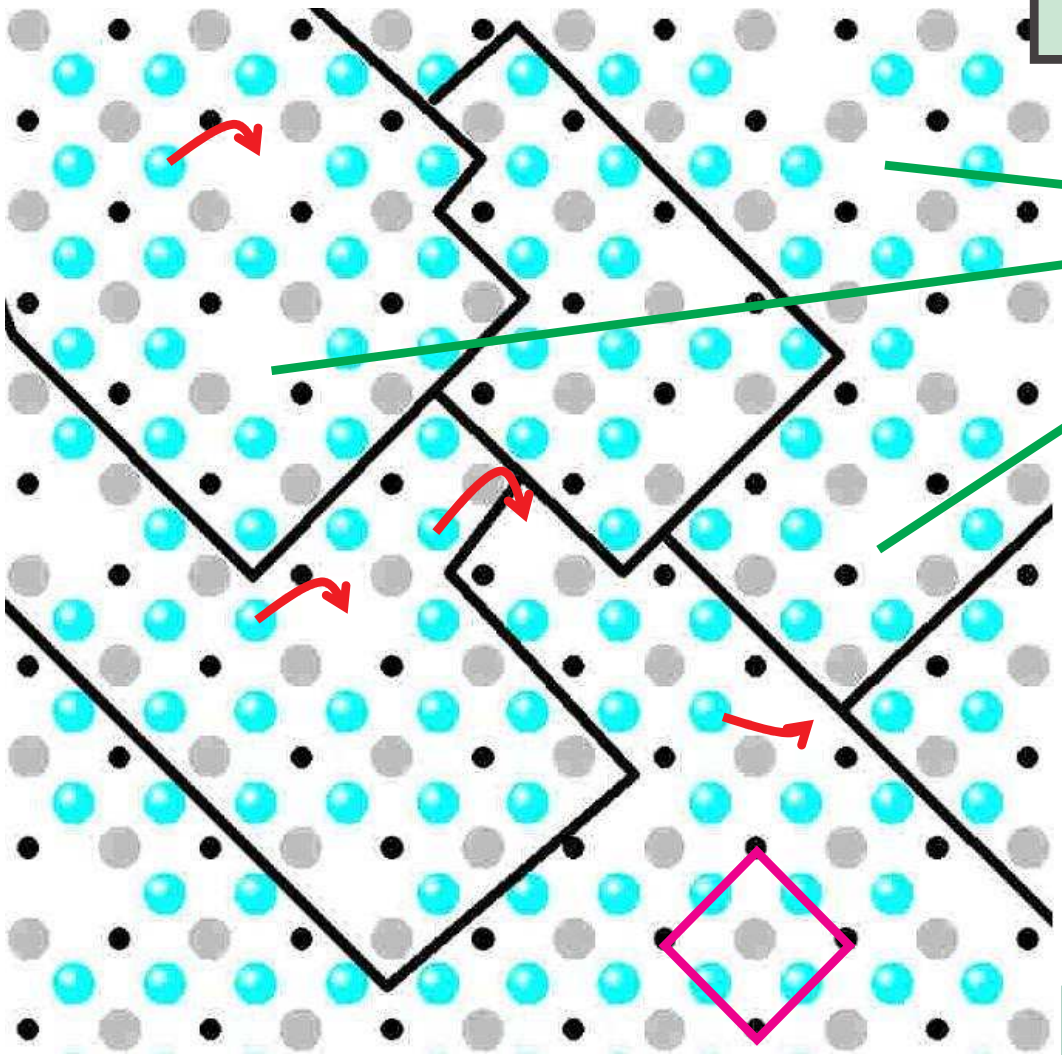
- Device for efficient conversion of chemical energy into electricity.



- SOFC cathode materials: ***fast oxygen conductivity & electronic conductivity.***

Effects of oxygen/vacancy ordering in cathode materials for SOFC:

Cubic – $La_xSr_{1-x}MnO_{3-\delta}$



Disordered oxygen vacancies

O^{2-} moving through low energy barriers

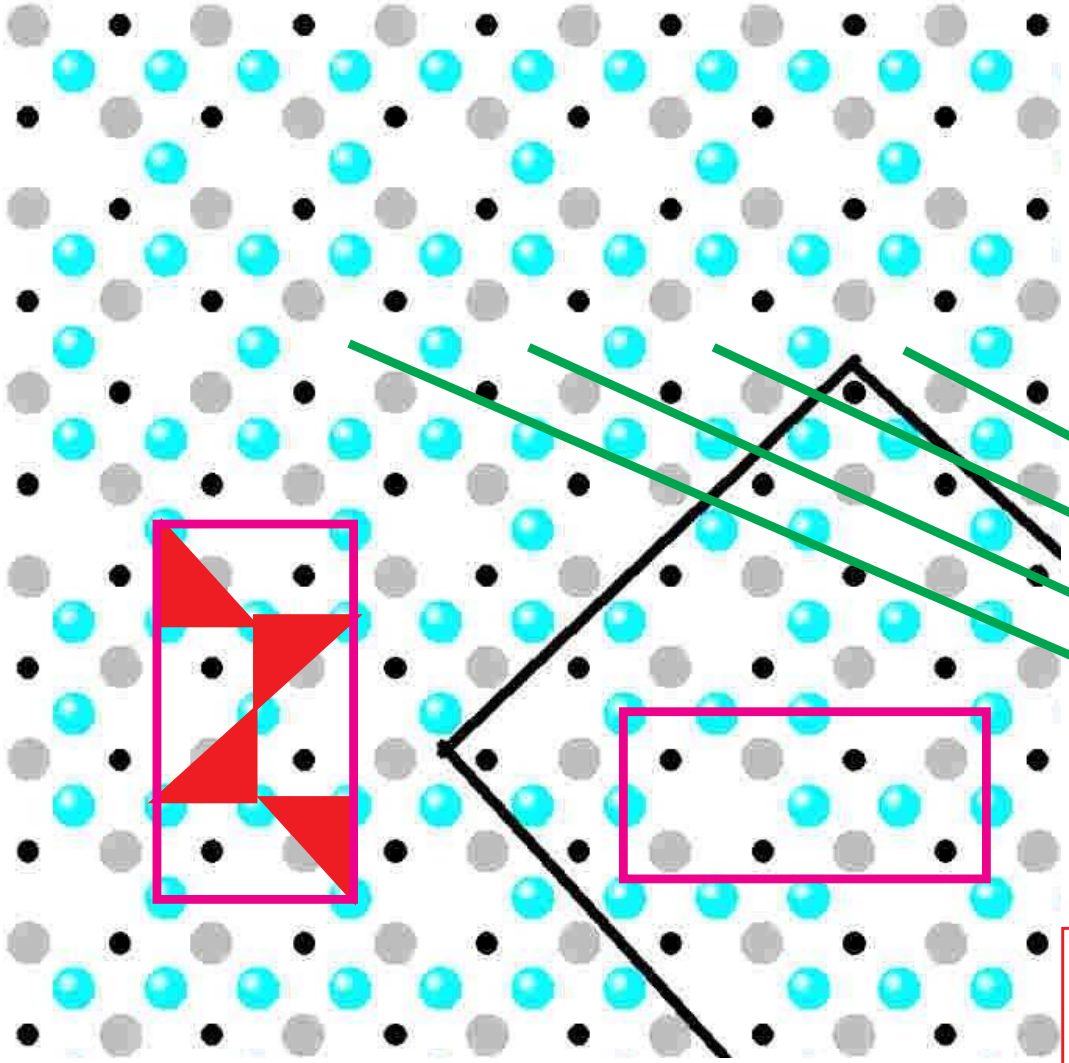
orbital disorder

Metallic character

FAST OXYGEN CONDUCTIVITY

ELECTRONIC CONDUCTIVITY

Effects of oxygen/vacancy ordering in cathode materials for SOFC:



$(La_xSr_{1-x})_2Mn_2O_5$
(ordered $La_xSr_{1-x}MnO_{2.5}$ phase)

ordered vacancies

Tightly bound oxygen vacancies

orbital ordering

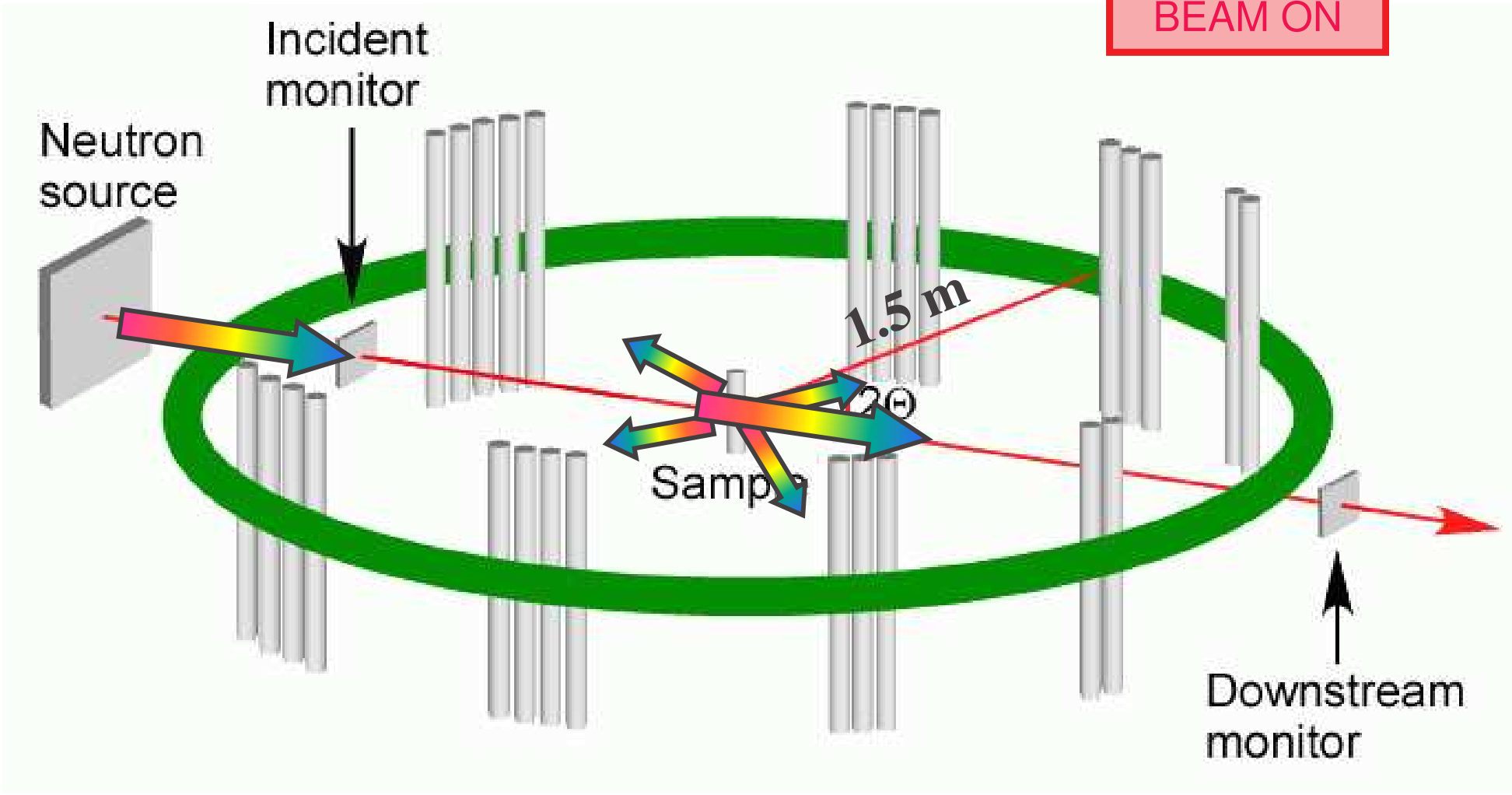
Insulating character

REDUCED OXYGEN CONDUCTIVITY

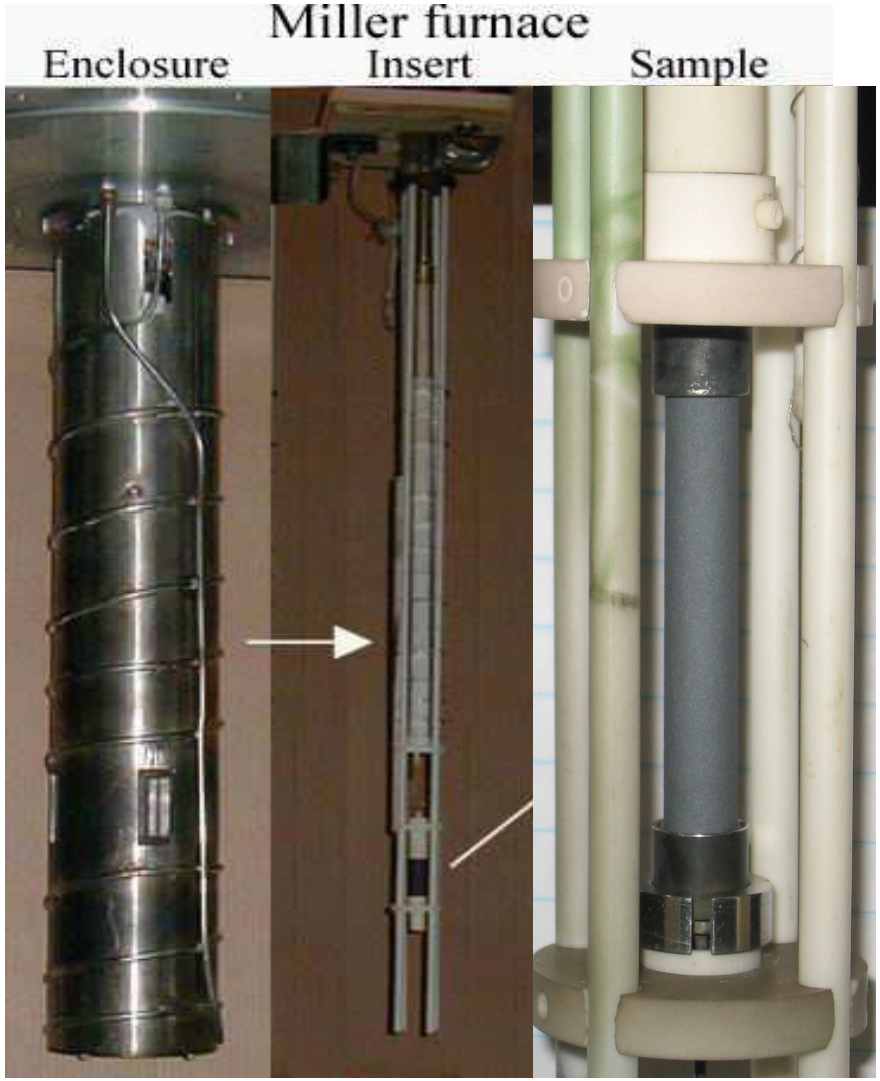
NO ELECTRONIC CONDUCTIVITY

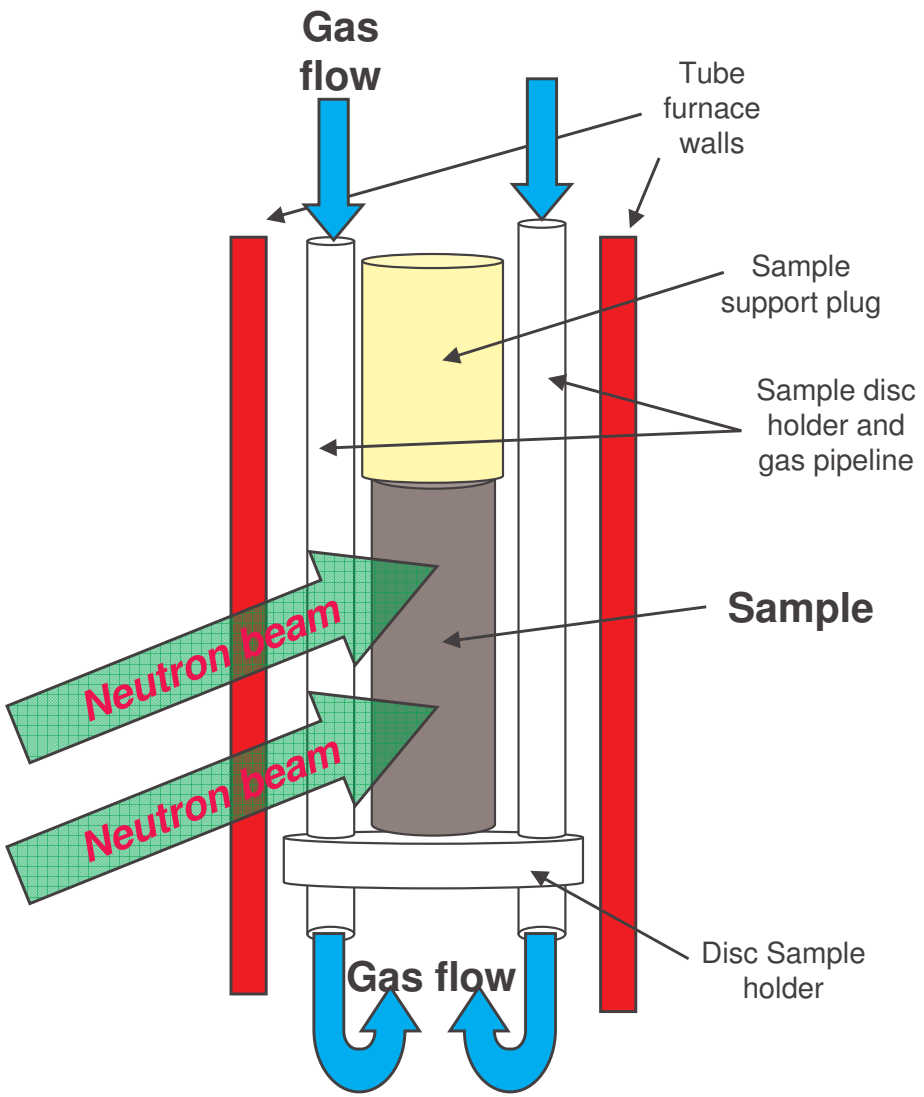
TOF Diffractometer Setup at former IPNS facility

Schematic Illustration of SEPD/GPPD



In-situ neutron diffraction experiment setup

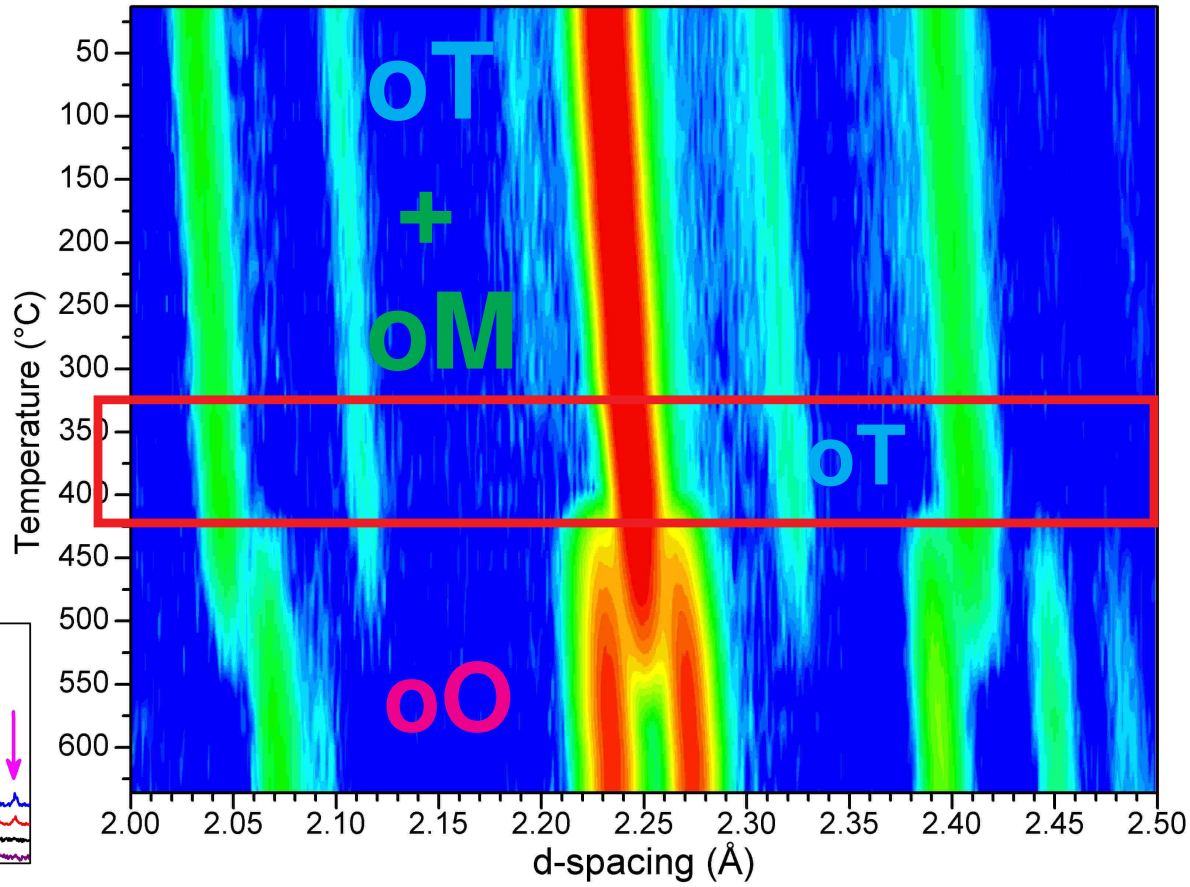


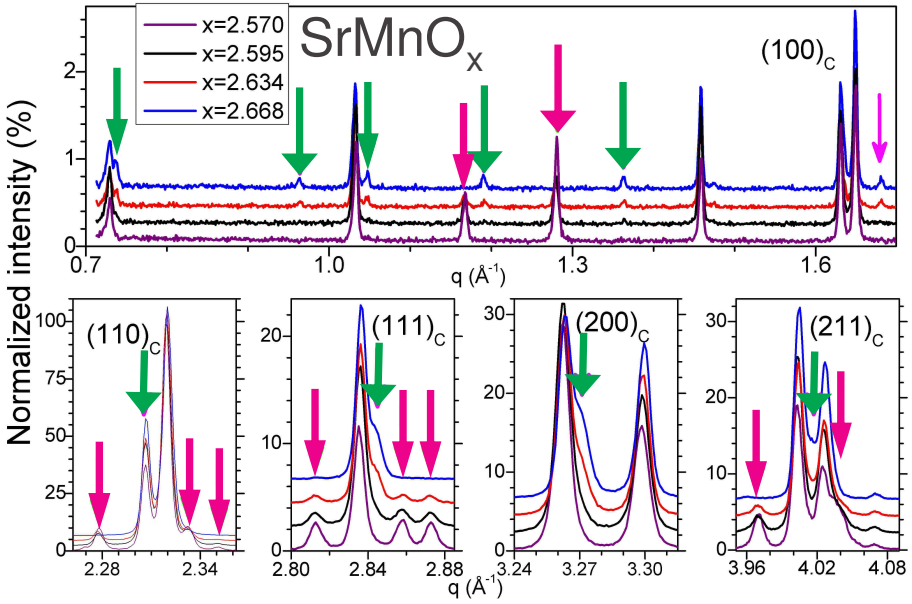


From RT to 1200 ℃ in O_2, Air, Ar, CO, CO_2, mixtures, etc. and var. flow rate.

$SrMnO_x$: In-situ NPD experiment

- Initial Interpretation: Starting sample looses oxygen and a phase transition occurs between vacancy ordered phases oT-$Sr_5Mn_5O_{13}$ and oO-$Sr_2Mn_2O_5$.

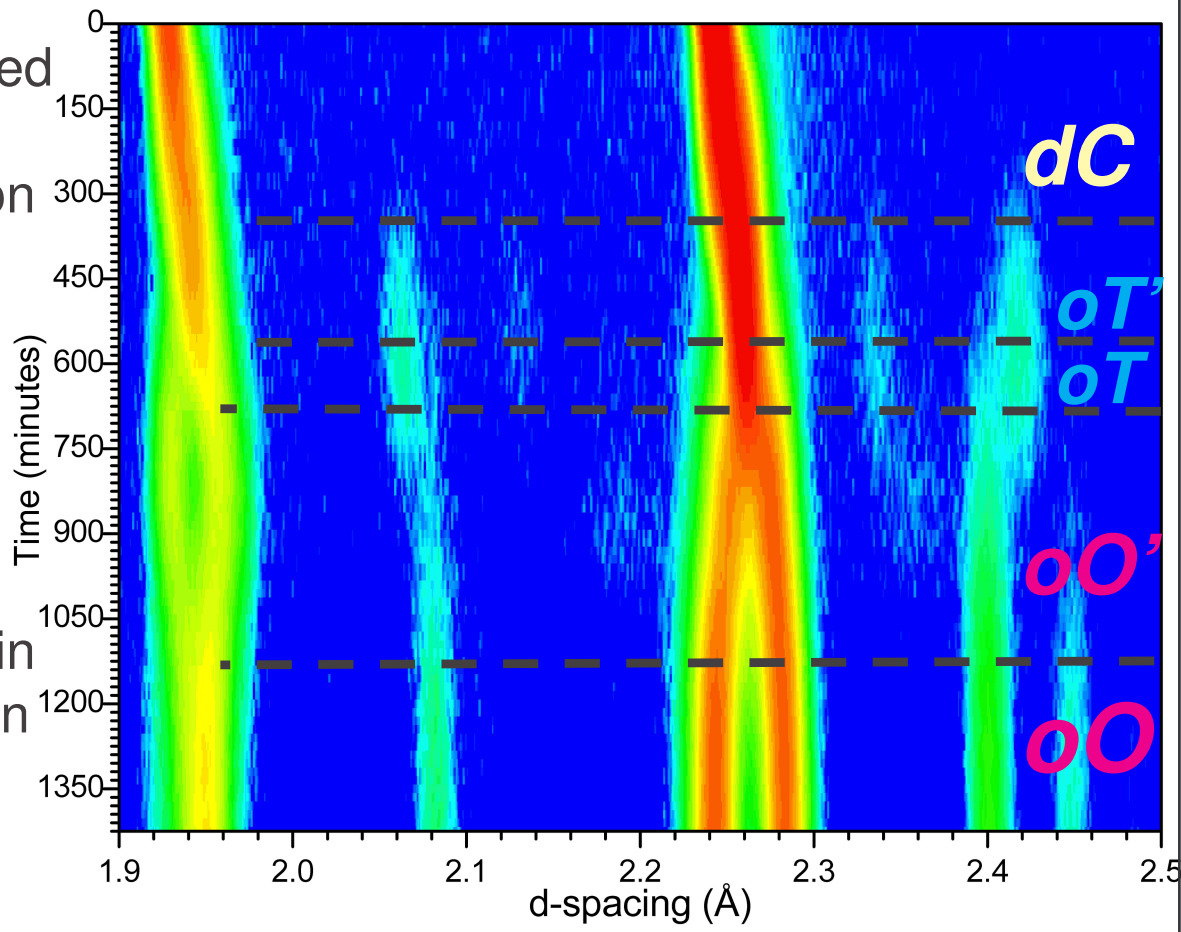




- Reality was more complex and required high-resolution X-ray diffraction (APS): Initial sample was two-phase, one of them never reported. The new phase oM-$Sr_7Mn_7O_{19}$ converts to $Sr_5Mn_5O_{13}$ just before $Sr_2Mn_2O_5$ starts forming.

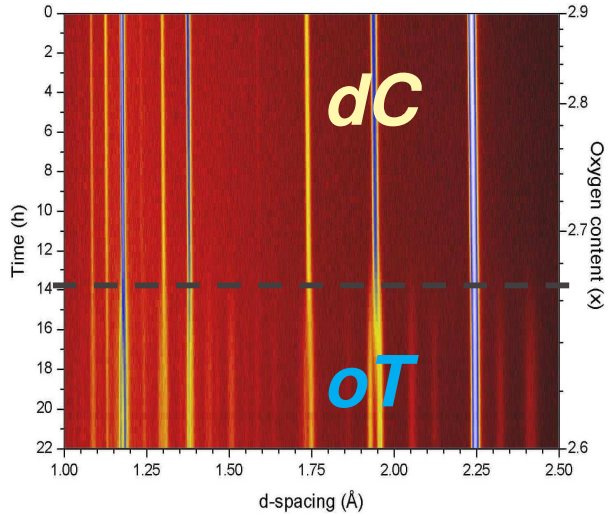
$La_{0.1}Sr_{0.9}MnO_x$: In-situ NPD experiment

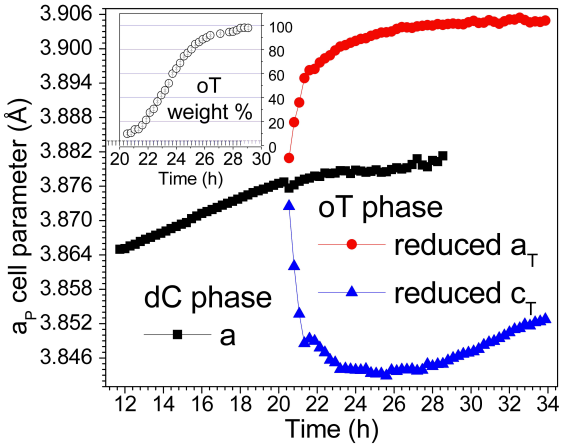
- Initial interpretation:
  Sample shows two vacancy ordered phases similar to oT and oO that forms consecutively upon reduction of oxygen content of initial cubic (vacancy-disordered) dC phase.
- Reality was again more complex:
  The oT and oO vacancy-ordering patterns are stable in the $La_{0.1}Sr_{0.9}MnO_x$ system. However, partial vacancy filling is observed in both cases leading to the formation of oT'-$(La_{0.1}Sr_{0.9})_5Mn_5O_{13+\delta}$ and oO'-$(La_{0.1}Sr_{0.9})_2Mn_2O_{5+\delta}$ closely related to original oT and oO.

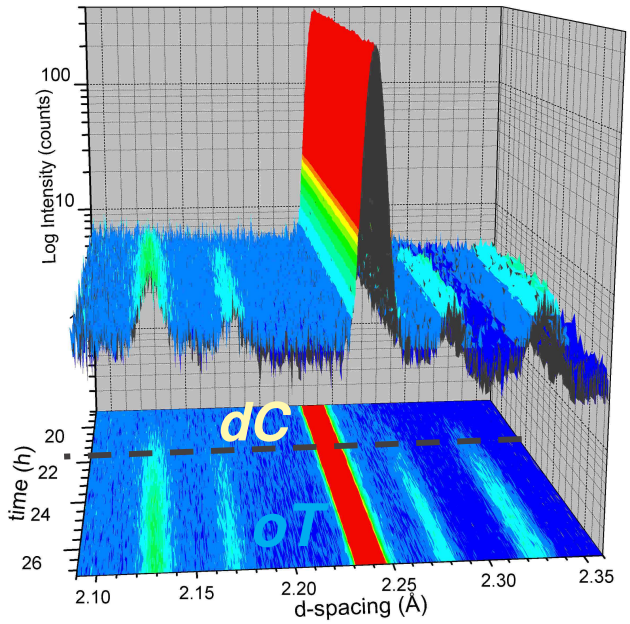


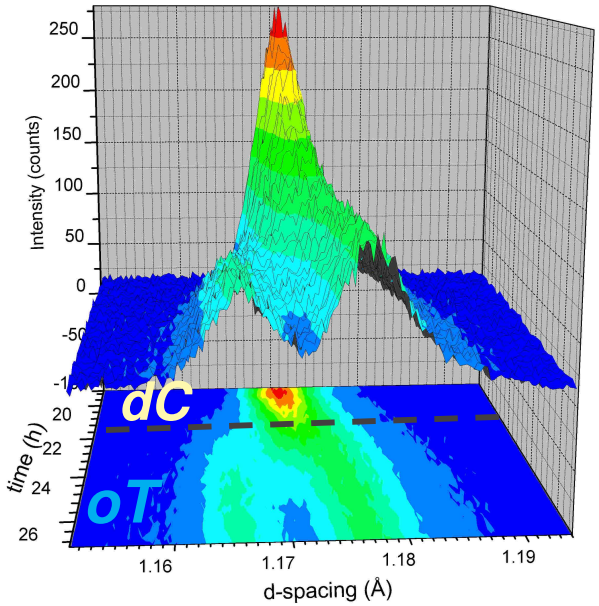
$La_{0.2}Sr_{0.8}MnO_x$: In-situ NPD experiment

- Initial (and final) interpretation: Simple cubic phase converts into ordered phase oT-$(La_{0.2}Sr_{0.8})_5Mn_5O_{13}$.
- However vacancy-ordered phase shows significant structural distortions that reduces it´s symmetry from tetragonal to monoclinic.
- The distortions are a consequence of a combination of orbital ordering with structural disorder.
- Further studies showed the existence of the phase oO-$(La_{0.2}Sr_{0.8})_2Mn_2O_5$

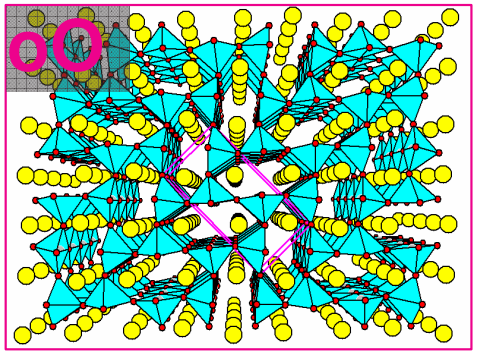


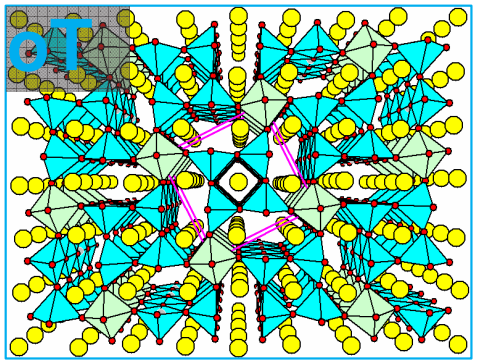


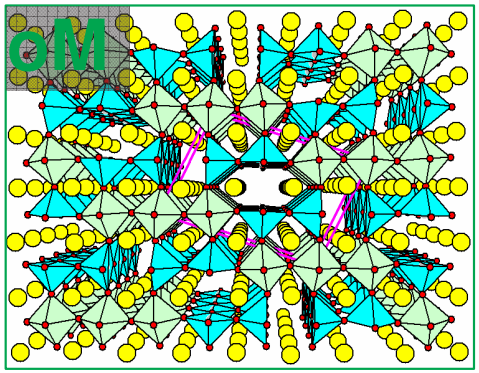


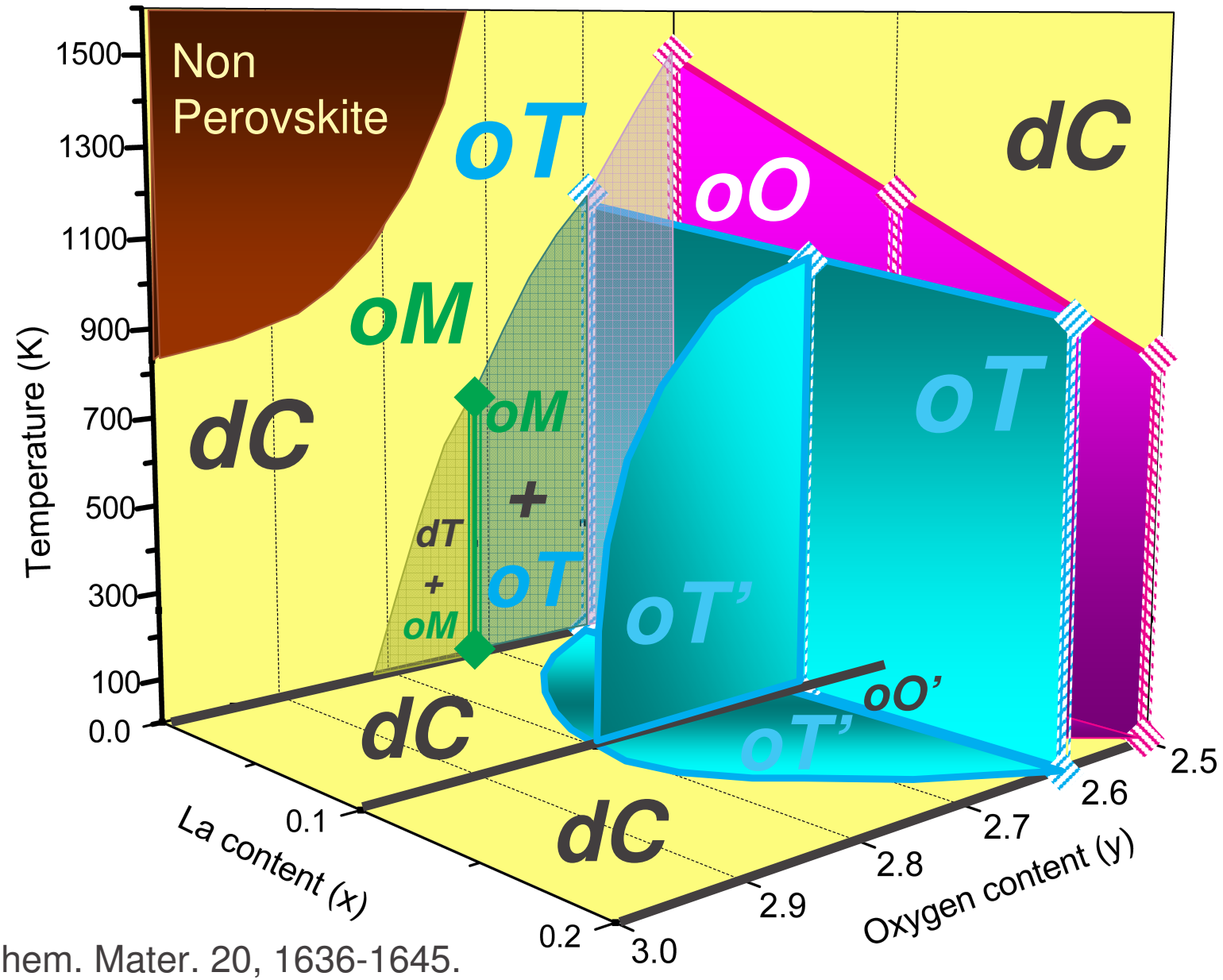


Composition-Temperature-Oxygen content phase diagram









Suescun L. et al, (2008) Chem. Mater. 20, 1636-1645.

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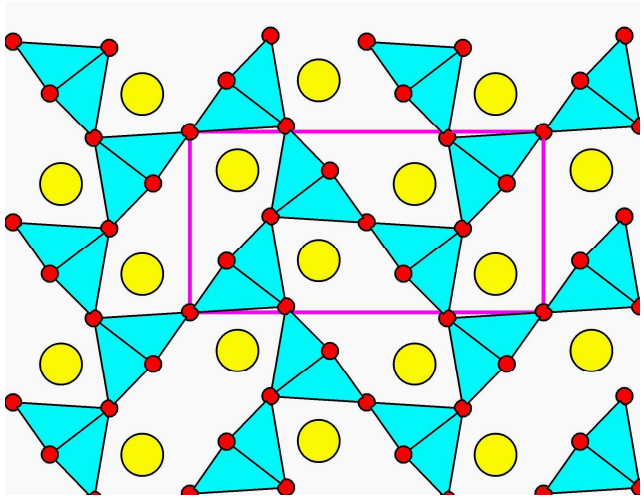
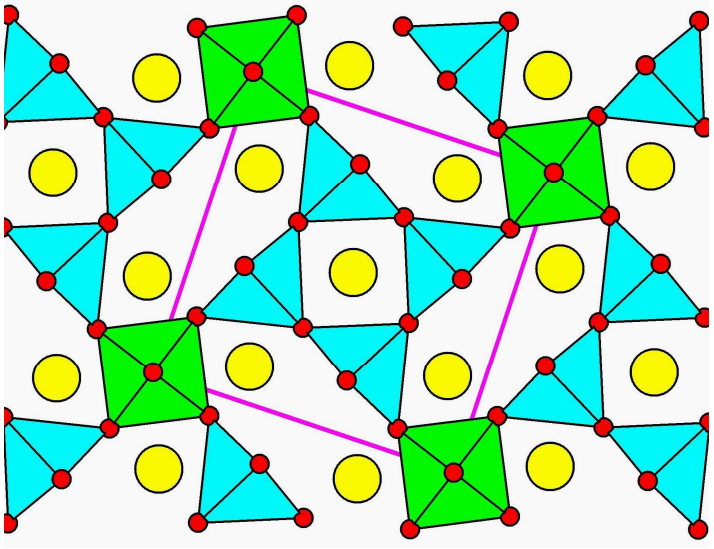
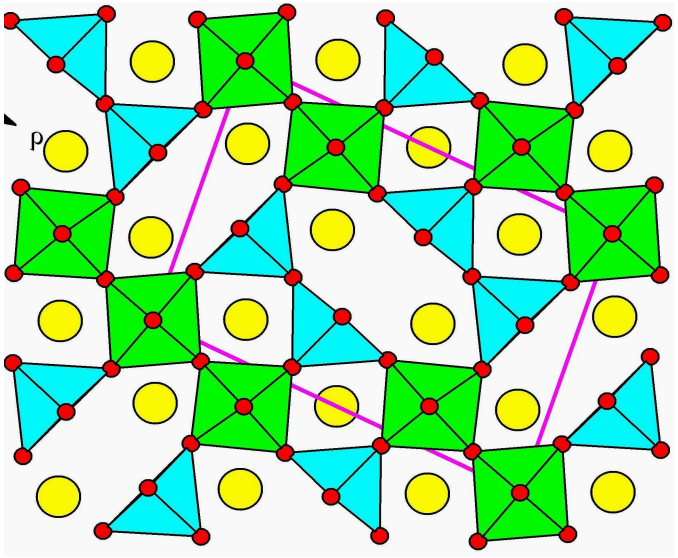
Charge ordering in $Sr_5Mn_5O_{13}$ and $Sr_7Mn_7O_{19}$



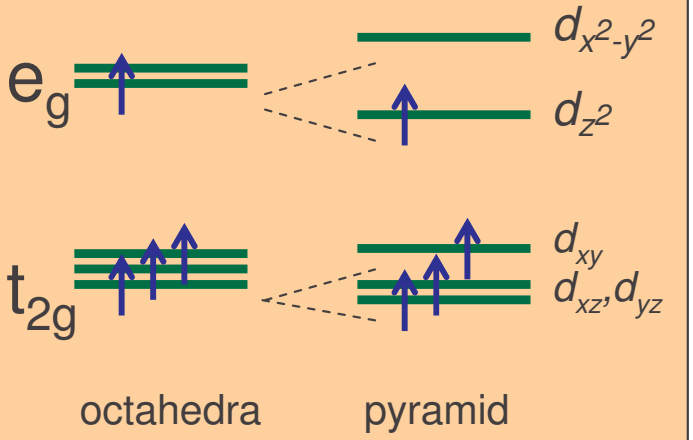




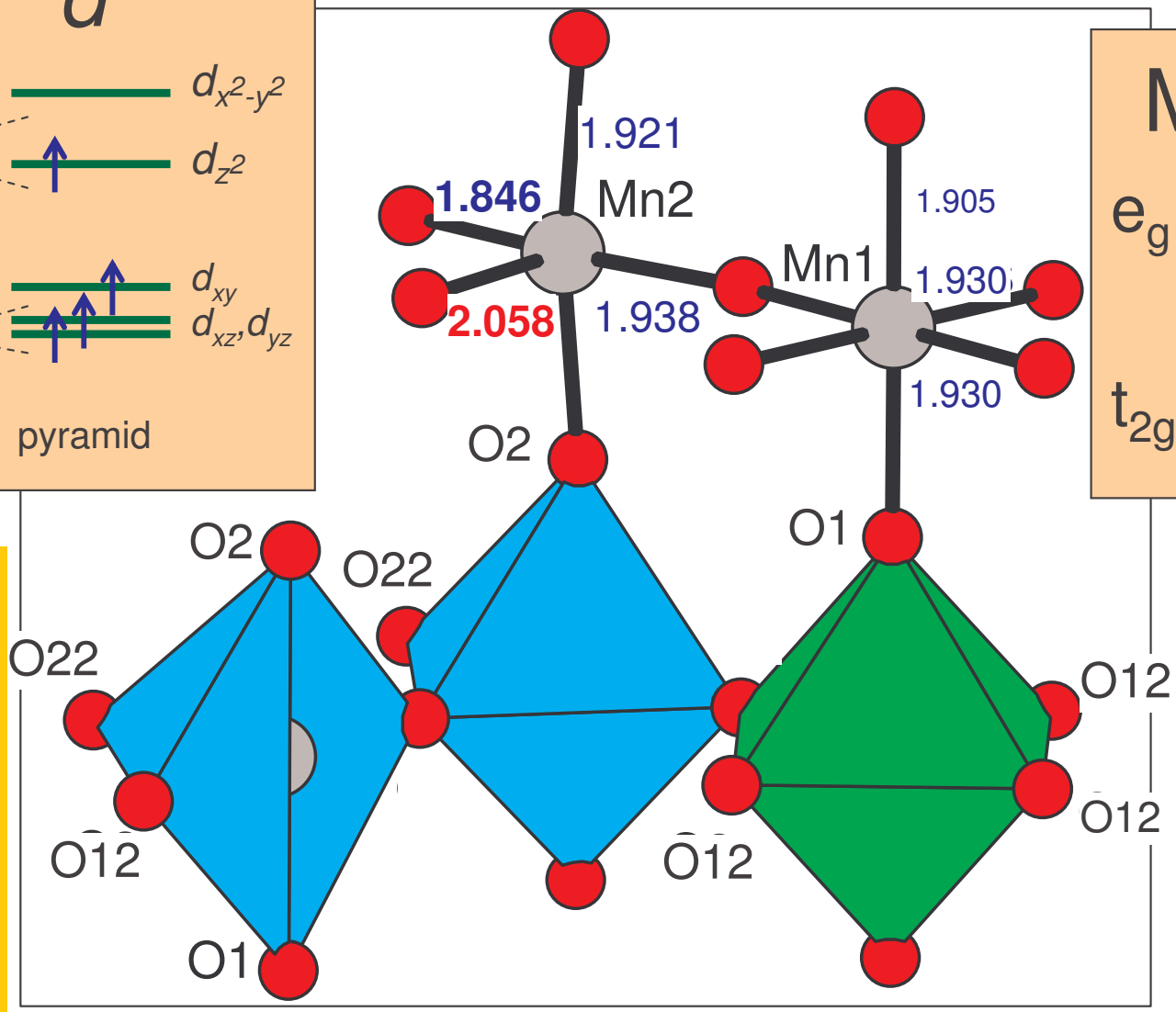
$Sr_2Mn_2O_5$	$Sr_5Mn_5O_{13}$	$Sr_7Mn_7O_{19}$
Mn^{3+} Pyramids	$Mn^{16/5+} = Mn^{3.2+}$ 4 Mn^{3+} P+ 1 Mn^{4+} O	$Mn^{24/7+} = Mn^{\sim 3.43+}$ 4 Mn^{3+} P+ 3 Mn^{4+} O
BVS: Mn1 3.08 (P)	BVS: Mn1 3.81(O) Mn2 3.15 (P)	BVS: Mn1 3.75 Mn2 4.00 (O) Mn3 3.16 Mn4 3.18 (P)
$Sr_4(Mn^{3+})_4O_{10}$	**$Sr_5(Mn^{3+})_4Mn^{4+}O_{13}$**	**$Sr_7(Mn^{3+})_4(Mn^{4+})_3O_{19}$**

Orbital ordering in $Sr_5Mn_5O_{13}$ and $Sr_7Mn_7O_{19}$

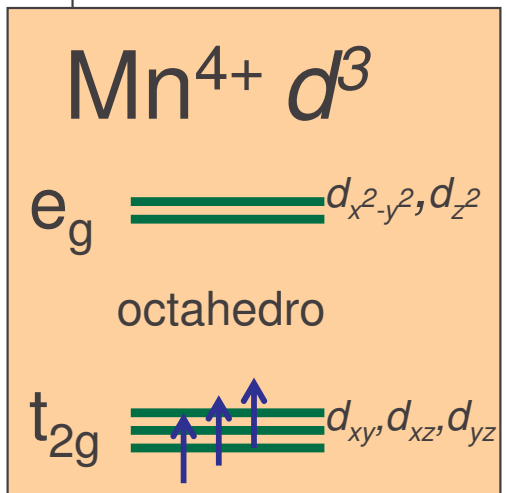
Mn^{3+} d^4



Jahn-Teller active Mn^{3+} cations (d^4) are located in elongated pyramids with d_{z^2} orbital along the apical direction



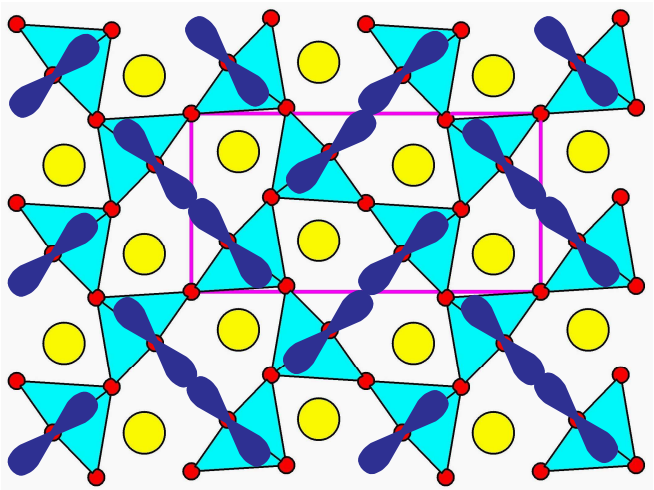
Mn^{4+} d^3



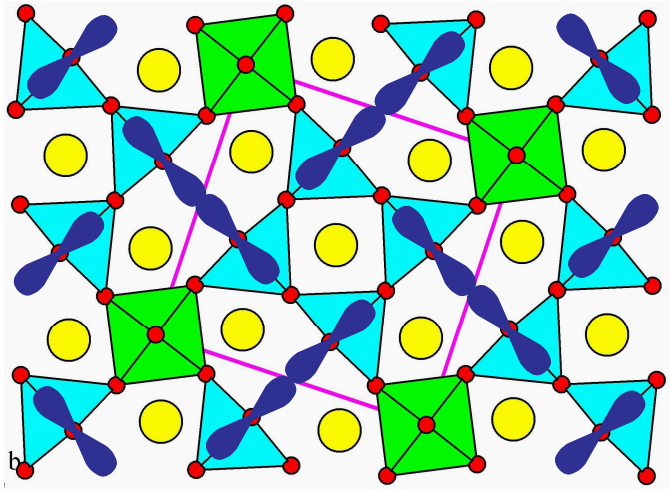
Non J-T Mn^{4+} (d^3) cations are located in slightly distorted octahedra

Orbital ordering in $Sr_5Mn_5O_{13}$ and $Sr_7Mn_7O_{19}$

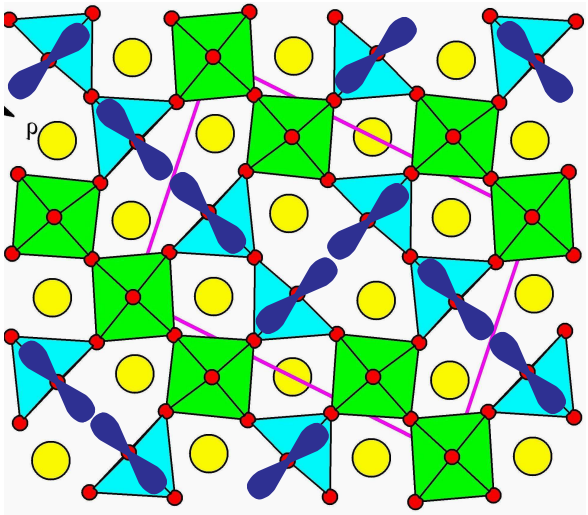
$Sr_2Mn_2O_5$



$Sr_5Mn_5O_{13}$



$Sr_7Mn_7O_{19}$



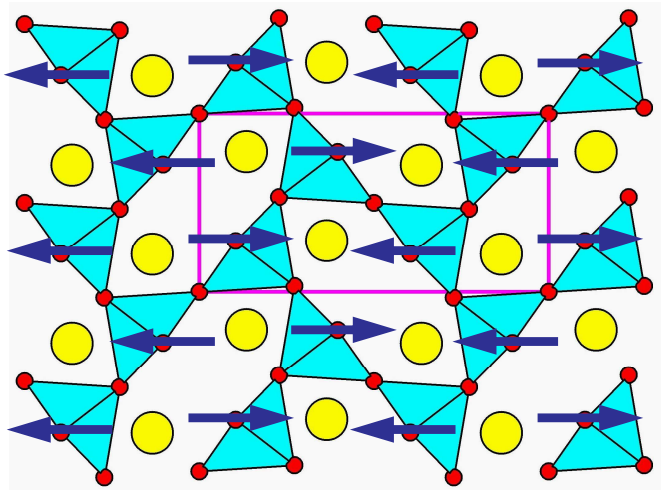
$Sr_2Mn_2O_5$	
Mn1	
O1 (×2)	1.9198(4)
O3	1.941(3)
O2a	2.063(3)
O2e	1.875(3)

$Sr_5Mn_5O_{13}$	
Mn2	
O2 (×2)	1.9212(5)
O12	1.938(5)
O22a	2.058(4)
O22e	1.846(4)

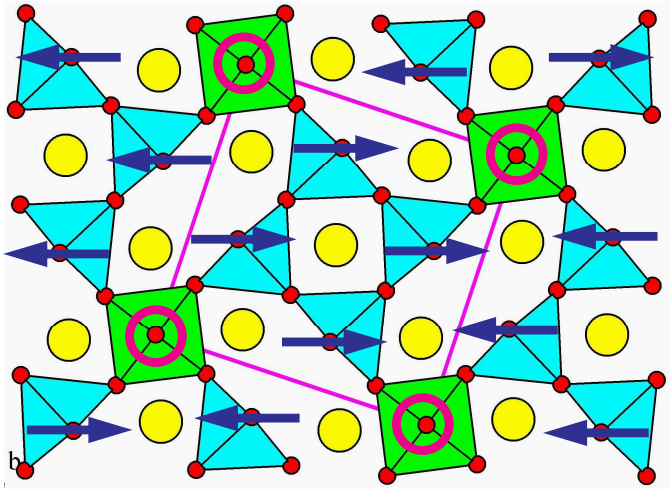
$Sr_7Mn_7O_{19}$			
Mn3		Mn4	
O3 (×2)	1.914(3)	O4 (×2)	1.908(2)
O23	1.96(2)	O42	1.96(2)
O34	1.99(2)	O24	2.02(3)
O13	1.88(3)	O34	1.86(2)

Magnetic ordering in $Sr_2Mn_2O_5$ and $Sr_5Mn_5O_{13}$

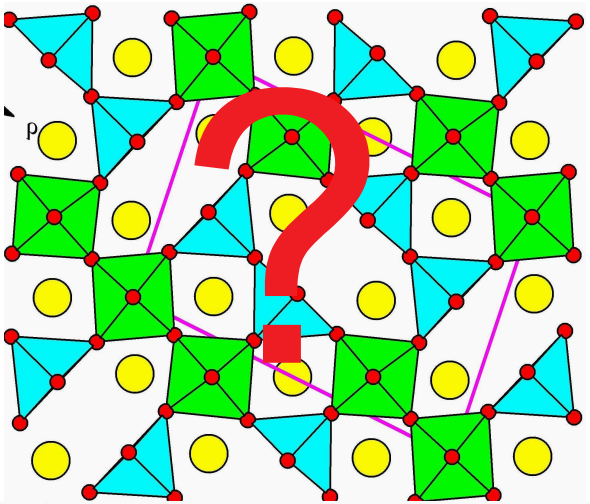
$Sr_2Mn_2O_5$

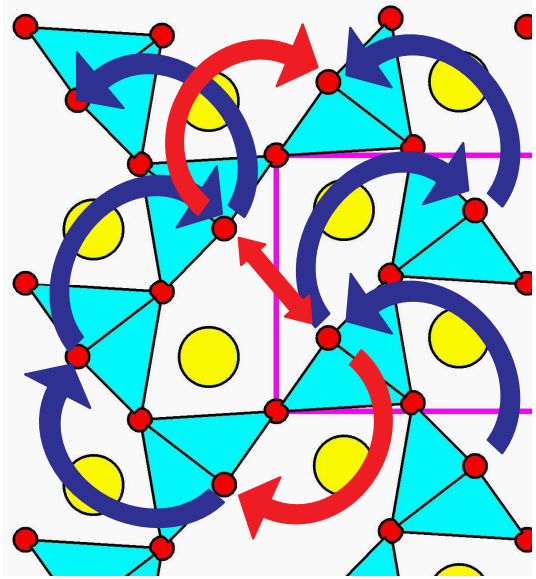


$Sr_5Mn_5O_{13}$



$Sr_7Mn_7O_{19}$



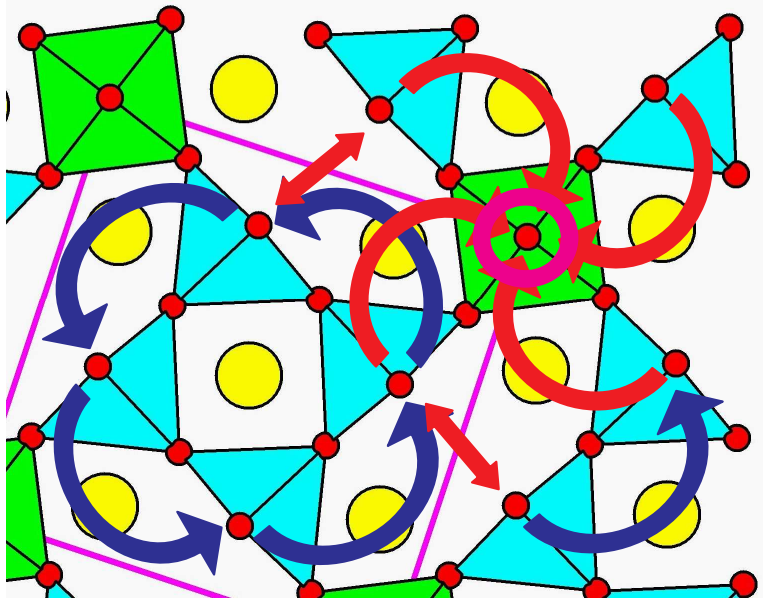


Complex exchange interactions make complex magnetic structures

Blue: Ferromagnetic

Red: Antiferromagn.

Pink: Frustration!!!!



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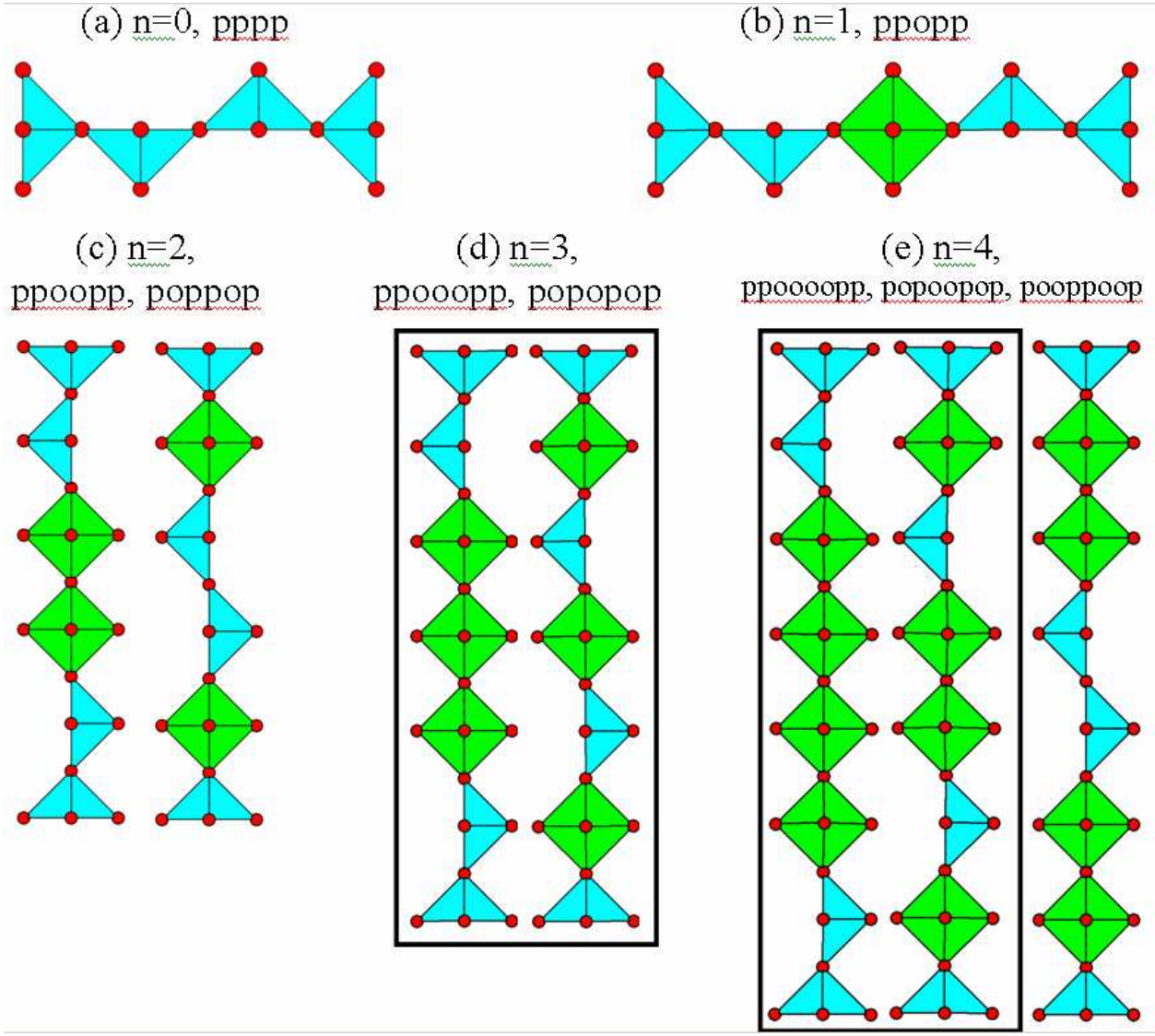
A new homologous series $Sr_{4+n}Mn^{3+}{}_4Mn^{4+}{}_nO_{10+3n}$

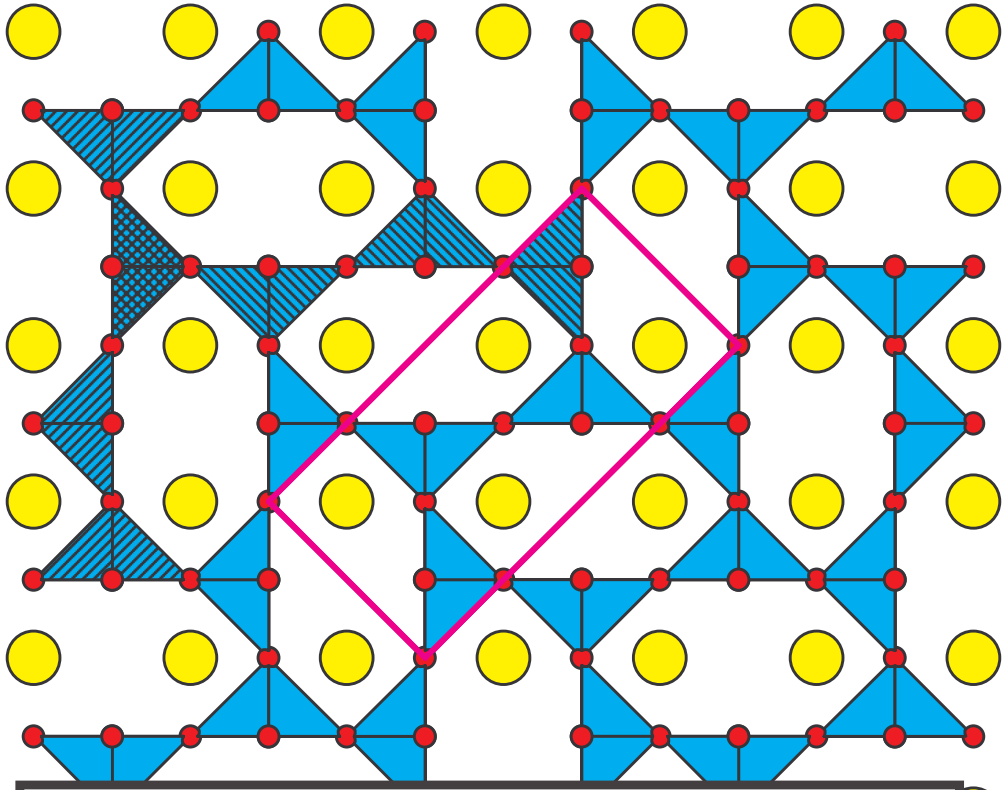
- Building blocks formed by 4 pyramids and n octahedra can be used to generate compounds in the series $Sr_{4+n}Mn^{3+}{}_4Mn^{4+}{}_nO_{10+3n}$
- Members of the series observed to date (n=0, 1 and 3) are formed by symmetrical blocks (the building block displays 2/m symmetry)
- For certain values of n different building blocks lead to different structures, but in some cases a unique pattern is formed that combines two blocks (boxes).
- No compound corresponding to non-unique structural models have been observed so far in the $SrMnO_x$ system.



Suescun L. & Dabrowski B. (2008) Acta Crystallographica Section B, 64, 177-186.

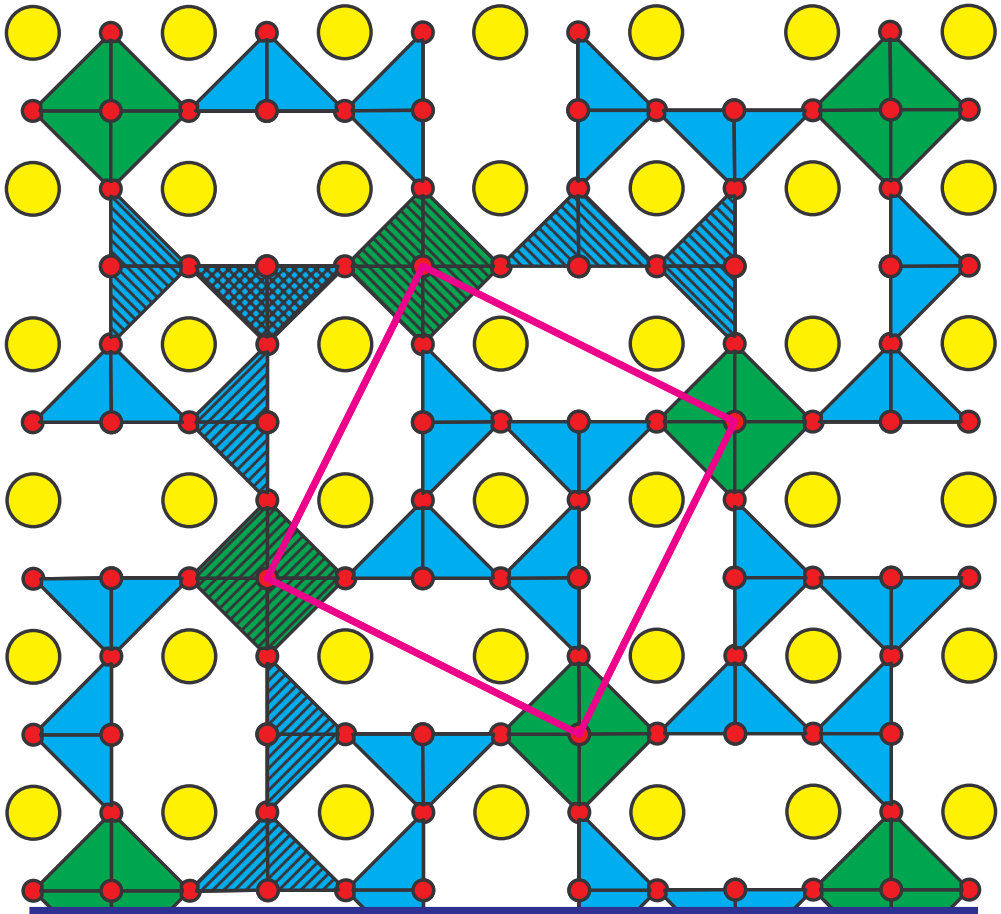
A new homologous series $Sr_{4+n}Mn^{3+}{}_4Mn^{4+}{}_nO_{10+3n}$

$Sr_4Mn_4O_{10}$ structure can be built based on n=0 block formed by 4 pyramids oriented along +x,-y,+y,-x along the lattice constants (or l.c. of them). The 4-pyramid pattern forms automatically in the orthogonal direction.



$Sr_{4+0}Mn^{3+}{}_4Mn^{4+}{}_0O_{10+3*0}=Sr_4Mn_4O_{10}$

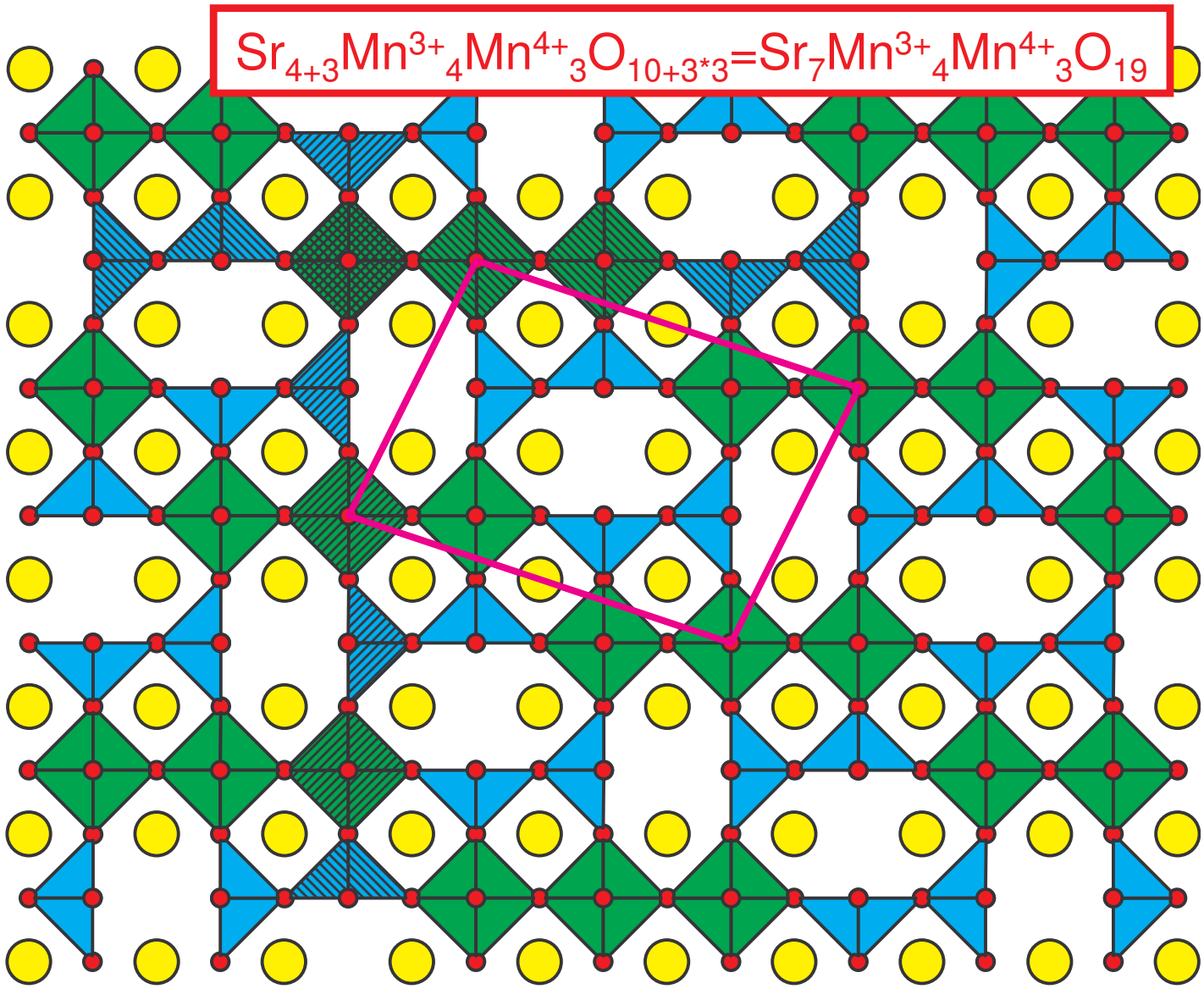
$Sr_5Mn_5O_{13}$ structure can be built based on the n=1 block containing 4 pyramids with one octahedron in the center



$Sr_{4+1}Mn^{3+}{}_4Mn^{4+}{}_1O_{10+3*1}=Sr_5Mn_5O_{13}$

A new homologous series $Sr_{4+n}Mn^{3+}{}_4Mn^{4+}{}_nO_{10+3n}$

$Sr_7Mn_7O_{19}$ structure can also be built in an analogous manner using a block containing 4 pyramids and 3 octahedra. If the three octahedra are located in the center of the array and the horizontal direction is chosen to build the structure another possible block with alternating pyramids and octahedra is formed in the orthogonal (vertical) direction and viceversa. Both blocks display a symmetrical pyramid/octahedra arrangement.



A new homologous series $Sr_{4+n}Mn^{3+}{}_4Mn^{4+}{}_nO_{10+3n}$

- Predicted compounds in the $Sr_{4+n}Mn^{3+}{}_4Mn^{4+}{}_nO_{10+3n}$ homologous series

n	x in ABO_x	Pyramid/octahedra	Cell parameters† (a, b, c, γ, V)	Space group (ideal)†
0	2.5	pppp	$2^{1/2}a_P$ $2(2)^{1/2}a_P$ a_P $4V_P$	*Pbam* (55)
1	2.6	ppopp	$5^{1/2}a_P$ $5^{1/2}a_P$ a_P $5V_P$	*P*4/*m* (83)
2	2.667	ppoopp	$2a_P$ $10^{1/2}a_P$ a_P $\gamma = 108.4$ $6V_P$	*P*2/*m* (10)
		poppop	$2^{1/2}a_P$ $3(2)^{1/2}a_P$ a_P $6V_P$	*Pbmm* (*Pmma*, 51)
3	2.714‡	ppooopp/popopop	$5^{1/2}a_P$ $10^{1/2}a_P$ a_P $\gamma = 98.2$ $7V_P$	*P*2/*m* (10)
4	2.75	ppoooopp/popoopop	$2(2)^{1/2}a_P$ $10^{1/2}a_P$ a_P $\gamma = 116.6$ $8V_P$	*P*2/*m* (10)
		pooppoop	$2^{1/2}a_P$ $4(2)^{1/2}a_P$ a_P $8V_P$	*Pbam* (55)

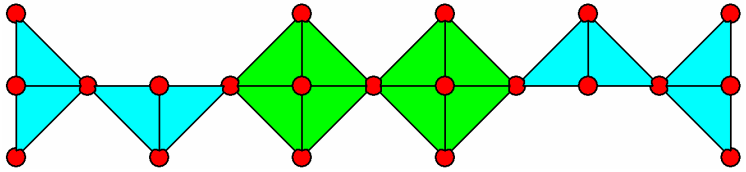
- Samples with composition $SrMnO_{2.667}$ (corresponding to n=2 member of the series) have been obtained as a mixture of $Sr_5Mn_5O_{13}$ ($SrMnO_{2.6}$, n=1) and $Sr_7Mn_7O_{19}$ ($SrMnO_{2.714}$, n=3).
- Samples with compositions $SrMnO_x$ 2.7<x<2.8 (oxygen content corresponding to n=3, n=4 and n=5) are a mixture of $Sr_7Mn_7O_{19}$ ($SrMnO_{2.714}$, n=3) and a vacancy-disordered phase with approximate composition $SrMnO_{2.82}$ (unpublished).

Suescun L. & Dabrowski B. (2008) Acta Crystallographica Section B, 64, 177-186.

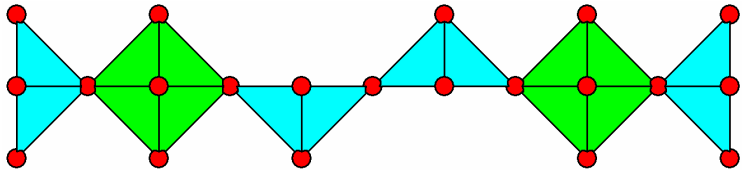
A new homologous series $Sr_{4+n}Mn^{3+}{}_4Mn^{4+}{}_nO_{10+3n}$

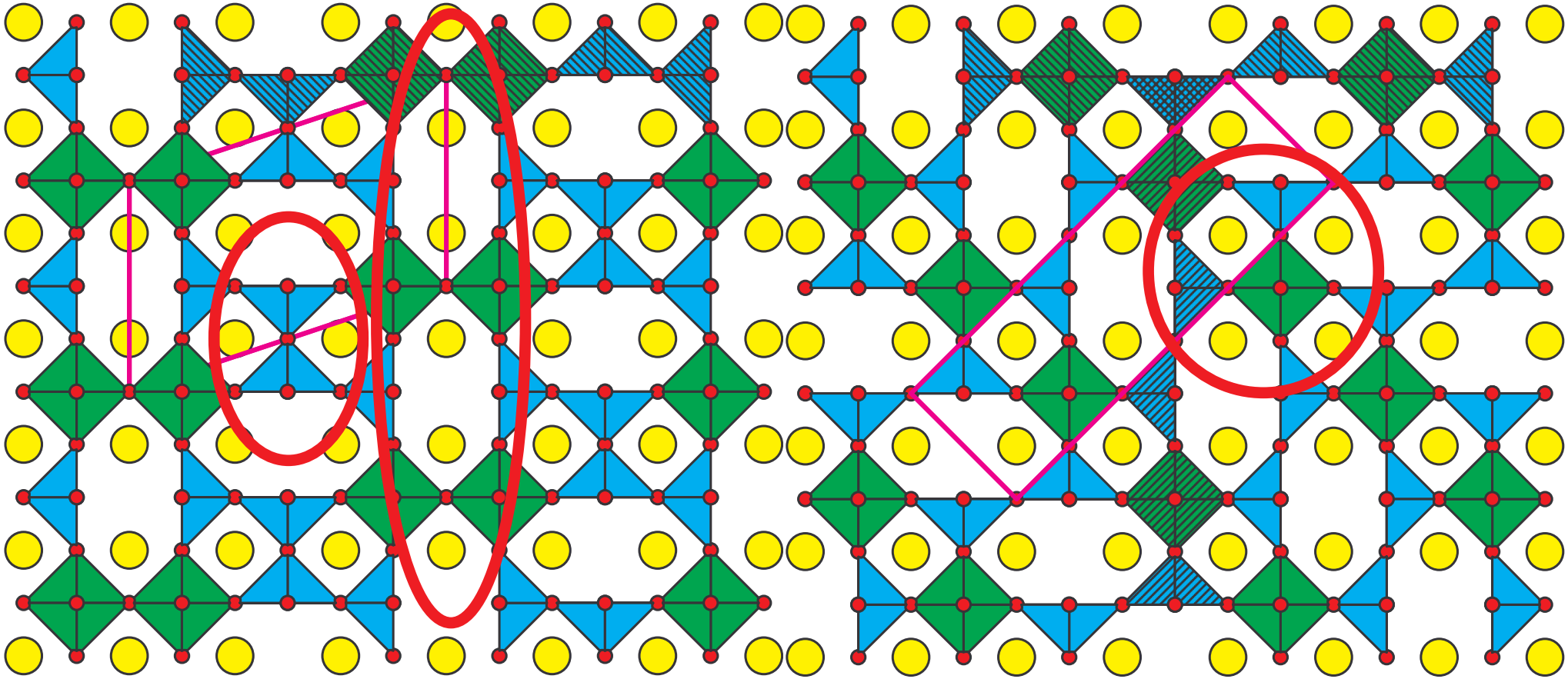
- Predicted compounds with n=2 ($Sr_6Mn^{3+}{}_4Mn^{4+}{}_2O_{16}$) show unfavorable features:

ppoopp-block



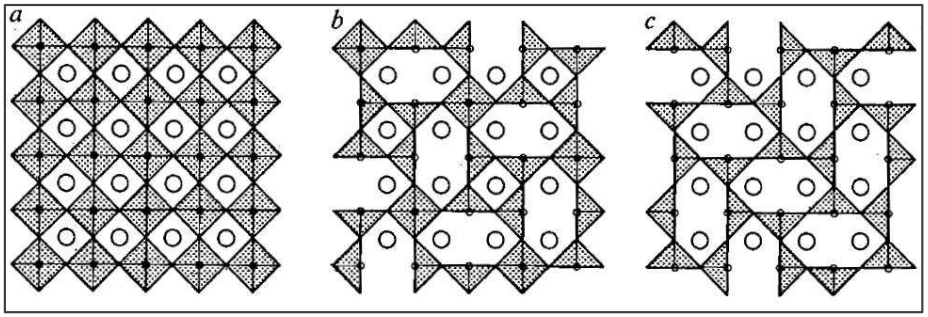
poppop-block





Other systems showing $A_{4+n}B_{4+n}O_{10+3n}$-type ordering:

$LaCuO_x$ & $NdCuO_x$ systems



- N=0 observed for d^9 Cu^{2+} (pyramids)
- N=1 observed for d^9 Cu^{2+} and d^8 Cu^{3+} (octahedra). Large monoclinic distortion observed
- No phases with N>2 observed

Bringley et al, *Letters to Nature* (1990) 347, 263-265
Chen et al, *Inorg Chem.* (1995) 34, 2077-2083.

$CaMnO_x$ system

- $Ca_2Mn_2O_5$ (N=0) structure has been determined
- HREM and ED studies of $CaMnO_{2.667}$ and $CaMnO_{2.75}$ have shown formation of local structures with unit cells compatible with those proposed for N=2 ($Ca_6Mn_6O_{16}$) and N=4 ($Ca_8Mn_8O_{22}$) members of the series respectively
- A neutron powder diffraction of $CaMnO_{2.75}$ was inconclusive possibly due to the coexistence of multiple ordering arrangements

Poeppelmeier et al *J. Solid State Chem.* (1982) 45, 79-79.
Reller et al *Proc. R. Soc. Lond. A* (1984) 349, 223-241.
Chiang & Poeppelmeier, *Mater Lett.* (1991) 12, 102-108.

Size and charge of A-site cation appears to play a key role in the stabilization of different structural patterns.

Conclusions

- New phases in the $La_xSr_{1-x}MnO_y$ system were found to display systematic structural trends like charge and orbital ordering of $Mn^{4+}O_6$ octahedra and $Mn^{3+}O_5$ elongated pyramids that allowed to formulate the new homologous series with general formula $Sr_{4+n}Mn^{3+}{}_4Mn^{4+}{}_nO_{10+3n}$ also observed in $CaMnO_x$ and La/$NdCuO_x$ systems.
- Oxygen-vacancy-ordering is directly related to charge and orbital ordering in manganites. The higher degree of disorder in the cation sublattice the more favorable the oxygen-vacancy-disordered phases and the lower the order-disorder transition temperature.

Take home message

- Don't get desperate for results (yet!). It takes patience, perseverance and maybe a bit of stubbornness.
- Enjoy it in any possible way, if results don't come and you get too frustrated with the science remember that you live ~ ½ hour drive away from one of the most beautiful cities in the world.
- Please, don't leave Chicagoland without visiting: Fermilab, The Field Museum of Natural History, Brookfield Zoo, Shed Aquarium, Adler Planetarium, Science and Industry Museum, Hads-on Science Museum (Aurora), Art Institue of Chicago, Navy Pier, Sears Tower, Hancock Building, Chicago Public Library, The Magnificent Mile, Millenium Park, Mexican Fine arts Museum, Lincoln Library and Museum (Springfield), Indiana Dunes, Wrigley Field, US Cellular Field, Soldier Field, Toyota Park, Bahai Temple (Evanston), Hindu Temple (Geneva), Winsconsin Dells, Downtown Naperville, Naper Settlement, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc, etc…

Perspectives

- Settle down in Uruguay
- Get all that unprocessed data published
- Visit Argonne before April 2009
- Continue performing experiments
  - In-situ NPD experiments at SNS
  - In-situ Synchrotron X-ray diffraction experiments at Brazilian Synchrotron Laboratory

Contributors to this work

- Bogdan Dabrowski & J.D. Jorgensen/Ray Osborn (supervisors)
- At Materials Science Lab. – Physics Department - NIU:
  - Konrad Świerczek, Omar Chmaissem (also at ANL)
  - Jim Mais, Steve Remsen, Ben Stillwell (synthesis, transport)
  - Stan Kolesnik (magnetism)
- At IPNS
  - SEPD staff: Simine Short, Joe Fieramosca, Ryoji Kiyanagi, Bob von Dreele
  - GPPD staff: Evan R. Maxey, Jim Richardson (RIP)
- At APS
  - Yang Ren (11 ID-C), Brian H. Toby, Jun Wang
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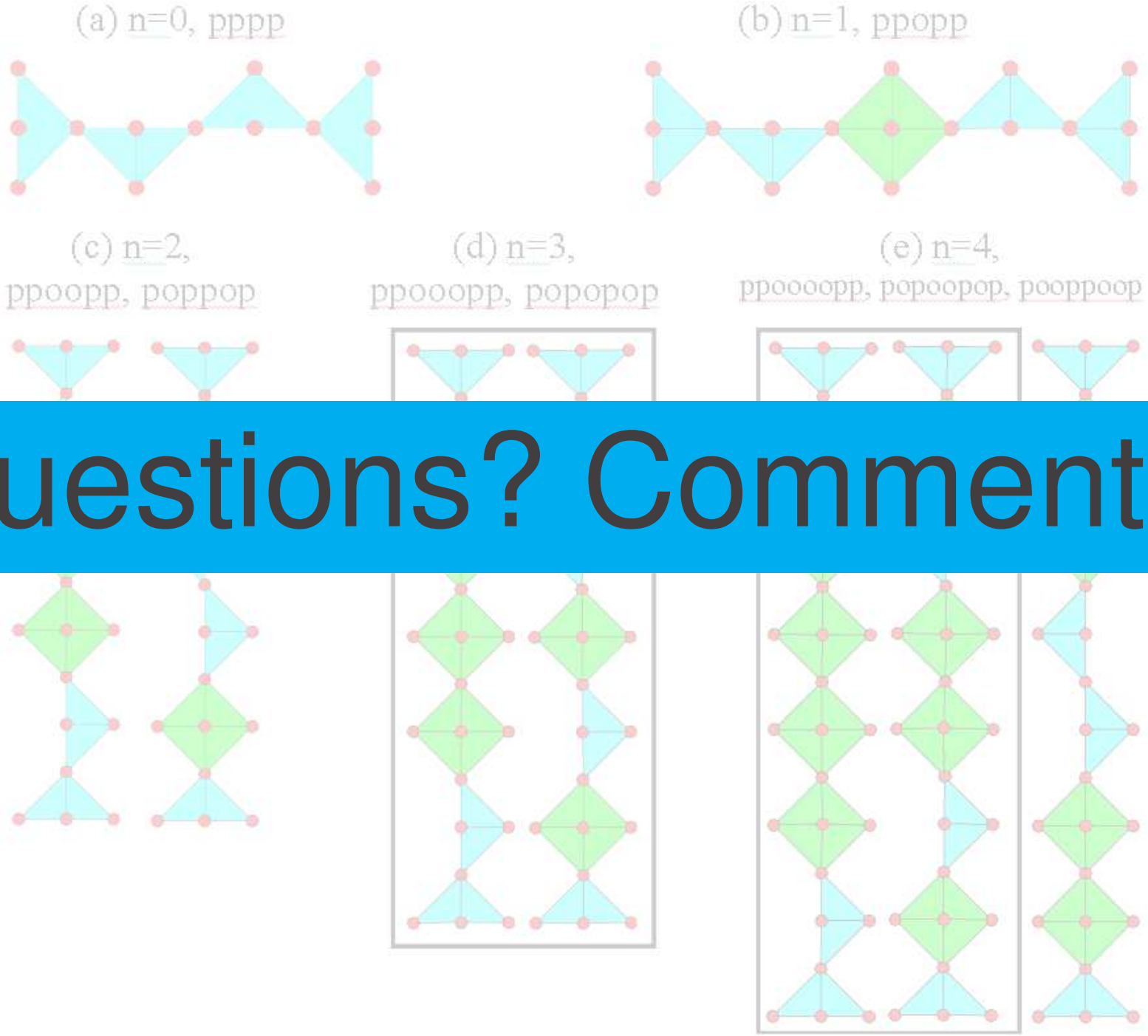
In memoriam

James D. Jorgensen, 1948 - 2006



Questions? Comments?