

# Structural and magnetic characterization of Sr<sub>1-x</sub>La<sub>x</sub>MnO<sub>y</sub> oxygen vacancy ordered phases (0<=x<0.4, 2.5<=y<2.75)



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Seminar at Institut Laue-Langevin, Grenoble, France May 14, 2012

#### **Geographical context**

#### Where do I come from



#### What are we known for

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#### Overview

- > Relevance of the  $La_xSr_{1-x}MnO_y$  system.
- SrMnO<sub>y</sub> perovskite phase stability, equilibrium phases and oxidation/reduction characteristics.
- Oxygen vacancy ordered phases (2.5<y<2.75), the Sr<sub>4+n</sub>Mn<sup>3+</sup><sub>4</sub>Mn<sup>4+</sup><sub>n</sub>O<sub>10+3n</sub> homologous series and La-doped Sr<sub>4+n</sub>Mn<sup>3+</sup><sub>4</sub>Mn<sup>4+</sup><sub>n</sub>O<sub>10+3n</sub>.
- Magnetic ordering in (La<sub>x</sub>Sr<sub>1-x</sub>)<sub>4</sub>Mn<sub>4</sub>O<sub>10</sub> and (La<sub>x</sub>Sr<sub>1-x</sub>)<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub> phases
- Perspectives.
- > Conclusions.

## Relevance of the La<sub>x</sub>Sr<sub>1-x</sub>MnO<sub>y</sub> system

Complex structural features and magnetic interactions

#### Mixed ionic-electronic conductor for SOFC cathodes



Chmaissem et al, PRB (2003) 67, 094431

## Relevance of the La<sub>x</sub>Sr<sub>1-x</sub>MnO<sub>y</sub> system

Challenging multi-step out-ofequilibrium synthesis for x<0.5



OO and enhanced magnetic interactions



5

## Stability of SrMnO<sub>v</sub> perovskite phases

 Negas and Roth (1970) and Mizutani et al (1970) describe equilibrium phases in the SrMnO<sub>v</sub> system:



- Cubic Perovskite SrMnO<sub>3</sub> metastable, converts to  $\alpha$  phase at ~600 °C.
- 4L Hexagonal α-SrMnO<sub>3</sub> loses oxygen and converts to oxygen-deficient perovskite at low pO<sub>2</sub> and high T (>1400 °C).
- Hexagonal SrMnO<sub>3- $\delta$ </sub> oxygen deficient forms of  $\alpha$ -SrMnO<sub>3</sub>.
- pseudo-cubic perovskite SrMnO<sub>2.694</sub> with orthorhombic unit cell.



Fig. 11. Isobar of SrMnO<sub>3 -  $\delta$ </sub> in air [66]; 4*L*-SrMnO<sub>3 -  $\delta$ </sub> =  $\alpha$ -SrMnO<sub>3 -  $\delta$ </sub>.

Negas T. & Roth R.S., JSSC 1 (1970) 409-418; Mizutani et al, J. Chem. Soc. Japan 73 (1970) 1103; Balakirev V.F. et al, Inorg. Mater 42 (2006) S49.

### Oxidation/reduction behavior of SrMnO<sub>v</sub>



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## Oxidation/reduction behavior of SrMnO<sub>v</sub>

- SrMnO<sub>2.25</sub> phase cannot be prepared by hydrogen reduction at 600 °C, a mixture of Sr<sub>2</sub>MnO<sub>3.5</sub> and MnO is obtained in such conditions.
- Preparation by very soft topotactic reduction under vacuum using NaH allowed to isolate this phase and related La-doped phases for the first time.
- SrMnO<sub>2.25</sub> adopts a layered form with Mn<sup>2+</sup> tetrahedra as in brownmillerite phase and Mn<sup>3+</sup> pyramids as in 112-type structures in a staggered distribution to keep an average Mn charge at 2.5+.



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- Magnetic ordering in (La<sub>x</sub>Sr<sub>1-x</sub>)<sub>4</sub>Mn<sub>4</sub>O<sub>10</sub> and (La<sub>x</sub>Sr<sub>1-x</sub>)<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub> phases
- Perspectives.
- ➤ Conclusions.

## Vacancy-ordered phases (2.5<y<2.75)

- SrMnO<sub>25</sub>
- Caignaet et al (1985): Preparation and structural refinement (X-rays) Mn<sup>3+</sup> in square-pyramidal coordination  $(Ca_2Mn_2O_5 \text{ type phase})$
- Caignaert (1997): Magnetic and nuclear structure from neutron data. Orbital ordering in Mn<sup>3+</sup> cations also proposed.



#### Orbital ordering



- Leligny et al (2003): conference report on phase  $Sr_5Mn_5O_{13}$  with  $BaLa_4Cu_5O_{13}$ tetragonal structure.
- Charge ordering of Mn<sup>3+</sup>/Mn<sup>4+</sup> proposed.

Caignaert V. et al, Mat. Res. Bull. 20 (1985) 479-484. V. Caignaert, J. Magn. Magn. Mater. 166 (1997) 117-123. Leligny et al (2003) Association Française de Cristallographie Meeting 14/May/2012



## Vacancy ordered phases SrMnO<sub>v</sub>, 2.5<y<2.75

- Using synchrotron x-ray and neutron powder diffraction data, phase composition of samples with y<2.714 was established.</p>
- Miscibility gaps between SrMnO<sub>2.5</sub> (Sr<sub>4</sub>Mn<sub>4</sub>O<sub>10</sub>), SrMnO<sub>2.6</sub> (Sr<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub>) and SrMnO<sub>2.714</sub> (Sr<sub>7</sub>Mn<sub>7</sub>O<sub>19</sub>) phases imply multi-phase samples at y≠2.5, 2.6 or 2.714.



## Vacancy-ordered phases (2.5<y<2.75)

- SrMnO<sub>2.714</sub>
- New phase with oxygen content 2.714=19/7 closely related to tetragonal SrMnO<sub>2.6</sub>.
- Monoclinic structure with:  $a \approx a_T \approx \sqrt{5}a_P$ ,  $b \approx \sqrt{2}a_T \approx \sqrt{10}a_P$ ,  $c \approx a_P$ ,  $\gamma \approx 98.2^\circ$
- Oxygen content consistent with 4Mn<sup>3+</sup> and 3Mn<sup>4+</sup> per unit cell.
- It has been impossible to prepare a pure sample of this phase.





Suescun & Dabrowski (2008) Acta B, 64 177-186., Dixon E. et al., Chem. Mater., 2012, 24 (8), pp 1486–1495

## Charge ordering in Sr<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub> and Sr<sub>7</sub>Mn<sub>7</sub>O<sub>19</sub>



#### Sr<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub>

Sr<sub>2</sub>Mn<sub>2</sub>O<sub>5</sub>

Mn<sup>3+</sup> Pyramids

**BVS:** Mn1 3.08 (P) **CHARDI:** Mn1 3.00 (P)

Sr<sub>4</sub>(Mn<sup>3+</sup>)<sub>4</sub>O<sub>10</sub>

Mn<sup>16/5+</sup> = Mn<sup>3.2+</sup> 4 Mn<sup>3+</sup> P+ 1 Mn<sup>4+</sup> O **BVS:** Mn1 3.81(O) Mn2 3.15 (P) **CHARDI:** Mn1 (O) 50% Mn<sup>4+</sup>/50% Mn<sup>3+</sup> Mn2 (P) 87.5% Mn<sup>3+</sup>/12.5% Mn<sup>4+</sup>

Sr<sub>5</sub>(Mn<sup>3+</sup>)<sub>4</sub>Mn<sup>4+</sup>O<sub>13</sub>?

#### Sr<sub>7</sub>Mn<sub>7</sub>O<sub>19</sub>

Mn<sup>24/7+</sup> = Mn<sup>-3.43+</sup> 4 Mn<sup>3+</sup> P+ 3 Mn<sup>4+</sup> O **BVS:** Mn1 3.75 Mn2 4.00 (O) Mn3 3.16 Mn4 3.18 (P) **CHARDI:** Mn1 & Mn2 (O) 50 & 60% Mn<sup>4+</sup> Mn3 & Mn4 (P) 67.5% Mn<sup>3+</sup>

Sr<sub>7</sub>(Mn<sup>3+</sup>)<sub>4</sub>(Mn<sup>4+</sup>)<sub>3</sub>O<sub>19</sub>?

14/May/2012

BVS: Brown I.D. (1992) Acta Cryst., B48, 553 CHARDI: Nespolo et al (2001) Acta Cryst. B57, 652-664.

## Orbital ordering in Sr<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub> and Sr<sub>7</sub>Mn<sub>7</sub>O<sub>19</sub>



## Orbital ordering in Sr<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub> and Sr<sub>7</sub>Mn<sub>7</sub>O<sub>19</sub>



Vacancy ordered phases with y>2.5 observed in the system share a common pattern of vacancies ordered in planes along (130) cubic perovskite direction separated from the next layer by 0 (y=2.5), 1 (y=2.6) or 3 (y=2.714) cubic unit cells along [010] direction.









Suescun L. et al, (2007) Acta Cryst. B 64, 177.

Predicted compounds in the Sr<sub>4+n</sub>Mn<sup>3+</sup><sub>4</sub>Mn<sup>4+</sup><sub>n</sub>O<sub>10+3n</sub> homologous series

п	$x$ in $ABO_x$	Pyramid/octahedra	Cell parameters† $(a, b, c, \gamma, V)$	Space group (ideal)†
0	2.5	рррр	$2^{1/2}a_{\rm P} \ 2(2)^{1/2}a_{\rm P} \ a_{\rm P} \ 4V_{\rm P}$	<i>Pbam</i> (55)
1	2.6	ppopp	$5^{1/2}a_{\rm P} \ 5^{1/2}a_{\rm P} \ a_{\rm P} \ 5V_{\rm P}$	<i>P4/m</i> (83)
2	2.667	рроорр	$2a_{\rm P} \ 10^{1/2}a_{\rm P} \ a_{\rm P} \ \gamma = 108.4 \ 6V_{\rm P}$ $2^{1/2}a_{\rm P} \ 3(2)^{1/2}a_{\rm P} \ a_{\rm P} \ 6V_{\rm P}$	P2/m (10) Pbmm (Pmma, 51)
3 4	2.714‡ 2.75	ppooopp/popopop ppooopp/popoopop pooppoop	$5^{1/2}a_{\rm P}  10^{1/2}a_{\rm P}  a_{\rm P}  \gamma = 98.2  7V_{\rm P}$ $2(2)^{1/2}a_{\rm P}  10^{1/2}a_{\rm P}  a_{\rm P}  \gamma = 116.6  8V_{\rm P}$ $2^{1/2}a_{\rm P}  4(2)^{1/2}a_{\rm P}  a_{\rm P}  8V_{\rm P}$	P2/m (10) P2/m (10) Pbam (55)

- Samples with composition SrMnO<sub>2.667</sub> (corresponding to n=2 member of the series) have been obtained as a mixture of Sr<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub> (SrMnO<sub>2.6</sub>, n=1) and Sr<sub>7</sub>Mn<sub>7</sub>O<sub>19</sub> (SrMnO<sub>2.714</sub>, n=3).
- Samples with compositions SrMnO<sub>x</sub> 2.7<x<2.8 (oxygen content corresponding to n=3, n=4 and n=5) are a mixture of Sr<sub>7</sub>Mn<sub>7</sub>O<sub>19</sub> (SrMnO<sub>2.714</sub>, n=3) and a vacancy-disordered phase with approximate composition SrMnO<sub>2.82</sub> (unpublished).



 Electron diffraction performed over sample SrMnO<sub>2.668</sub> shows the coexistence of n=1 and n=3 phases coherently grown in the same crystallites (with a common orientation of the c axis) verifying that there is a miscibility gap between both phases (no solid solution possible) and that n=2 phases do not form even in the local scale.



Phase intergrowth between n=1 and n=3 phases is a consequence of the presence of planes of vacancies along 130 perovskite crystallographic planes in all the compounds in the homologous series as observed in HR-TEM images.



# Diagram of metastable phases in the SrMnO<sub>v</sub> system



 $La_{0.1}Sr_{0.9}MnO_{v}$  and  $La_{0.2}Sr_{0.8}MnO_{v}$ 

In-situ neutron time-offlight experiments were performed on La doped samples:

► La<sub>0.1</sub>Sr<sub>0.9</sub>MnO<sub>y</sub> (2.5<y<3): Similar oT and oO phases found in SrMnO<sub>y</sub> system.
La substitution promotes partial ocupation of vacant sites forming oT'-(La<sub>0.1</sub>Sr<sub>0.9</sub>)<sub>5</sub>Mn<sub>5</sub>O<sub>13+δ</sub> (δ<1) and oO'-(La<sub>0.1</sub>Sr<sub>0.9</sub>)<sub>2</sub> Mn<sub>2</sub>O<sub>5+δ</sub> (δ<0.5) isostructural with oT and oO phases respectively.



>La<sub>0.2</sub>Sr<sub>0.8</sub>MnO<sub>y</sub> (2.5<y<3) also shows similar phases oT and oO, but, as in SrMnO<sub>y</sub> system no partial vacancy filling is observed in either case.





## Selective doping in (La<sub>x</sub>Sr<sub>1-x</sub>)<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub>, x=0.0-0.3



Mn in pyramids remains 3+ and orbital-ordered, Mn in octahedron evolves from 4+ (x=0) to 2.5+ (x=0.3).
 Size of octahedral Mn restricted in z by fixed size of pyramidal arrangement.
 Mn<sup>3+</sup> in (La<sub>0.2</sub>Sr<sub>0.8</sub>)<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub> in compressed octahedral environment.

•Either inverted *e*<sub>g</sub> orbital ocupation...

 Or disordered elongated pyramids 14/May/2012



## Compressed Mn<sup>3+</sup> octahedra in (La<sub>0.2</sub>Sr<sub>0.8</sub>)<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub>



Inverted orbital occupancy should keep tetragonal symmetry but (La<sub>0.2</sub>Sr<sub>0.8</sub>)<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub> shows a monoclinic (pseudo-tetragonal) P2/m S.G.
 Disordered LaMnO<sub>3</sub>-like Mn<sup>3+</sup> octahedra would explain symmetry reduction and evidences of SRO in the compound (superstructure peaks broadening).

<sup>14/May/2012</sup> Suescun L. et al, JSSC 182 (2009) 187-195.

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- Magnetic ordering in (La<sub>x</sub>Sr<sub>1-x</sub>)<sub>4</sub>Mn<sub>4</sub>O<sub>10</sub> and (La<sub>x</sub>Sr<sub>1-x</sub>)<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub> phases
- Perspectives.
- > Conclusions.

# Magnetic characterization of $(La_x Sr_{1-x})_4 Mn_4 O_{10}$



- Sr<sub>4</sub>Mn<sub>4</sub>O<sub>10</sub> antiferromagnetic T<sub>N</sub>=380 K. There is a strong magnetic coupling between Mn<sup>3+</sup> centers.
- First magnetic structure determination by Caignaert V. (1997) using irreps analysis and Goodenough-Kanamori rules to discard improbable solutions: G<sub>x</sub>A<sub>y</sub> ordering proposed.
- Recent neutron thermo-diffraction studies suggest  $G_x$  component was spurious and  $A_y$  ordering is kept.
- Magnetic structure refinement in Shubnikov P<sub>c</sub>bam magnetic space group with a<sub>m</sub>=a, b<sub>m</sub>=b, c<sub>m</sub>=2c and final µ<sub>Mn</sub> ≈3.5 µ<sub>B</sub> a 40K.



2.0 ł 1.5 moment 1.0 0.5 0.0 -0.5 Av 2.0 1.5 1.0 0.5 0.0 50 100 150 200 250 300 350 400 450 Temperature (K)

Fig. 7. Fitted neutron patterns of  $Se_2Mn_2O_5$  (sample E) at 40 K using the  $P_1$ -ham symmetry model and the Ay arrangement of moments. The inset shows a detail of the low q data (Bonk 3). The purely structural peaks are shown in the top row of tick-marks while the magnetic ones in the bottom tow.

Caignaert V. (1997) JMMM 166, 117. Suescun L. et al (2007) JSSC 180, 1698. GxAy

## Magnetic characterization of (La<sub>x</sub>Sr<sub>1-x</sub>)<sub>4</sub>Mn<sub>4</sub>O<sub>10</sub>

Magnetic coupling among Mn cations follow simple exchange rules proposed by Goodenough-Kanamori:



 $> J_4$  direct exchange AF







## Magnetic characterization of (La<sub>x</sub>Sr<sub>1-x</sub>)<sub>4</sub>Mn<sub>4</sub>O<sub>10</sub>

Magnetic moment per atom decays with x without change in the magnetic structure as a consequence of addition of Mn<sup>2+</sup> randomly distributed over Mn<sup>3+</sup> sites.





## Magnetic characterization of (La<sub>x</sub>Sr<sub>1-x</sub>)<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub>

- Sr<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub> tetragonal, P4/m with 5 Mn per unit cell.
- No sample with exact stoichiometry SrMnO<sub>2.6</sub> and single phase could be prepared.
- The closest composition SrMnO<sub>2.595</sub> contains small quantities of  $Sr_4Mn_4O_{10}$  (16%) and  $Sr_7Mn_7O_{19}$  (9%).
- In all samples there is a broad feature ~280-300 K that appear to be T<sub>N</sub> and low temperature behavior suggest AF ordering of spins.
- Signal from  $Sr_4Mn_4O_{10}$  is clearly visible in all  $\chi$  vs T curves.



#### Indexing of magnetic peaks of Sr<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub> at 10 K



Playing again with the G-K rules for the new configuration of pyramids as in Sr<sub>4</sub>Mn<sub>4</sub>O<sub>10</sub> plus one Mn octahedron (expected to be mostly Mn<sup>4+</sup>) a magnetic structure can be proposed.









- ➤ This magnetic structure requires  $a_m = b_m = \sqrt{2} a \& c_m = 2c$  since magnetic coupling in z is also AF as in Sr<sub>4</sub>Mn<sub>4</sub>O<sub>10</sub>.
- All spins lay in the x-y plane and they are all up or down, no 90° rotation so the 4-fold symmetry is lost while the m and 2-fold magnetic inversion symmetry hold.
- k=(1/2,1/2,1/2) respect to the nuclear cell.
- Very difficult to resolve automatically since octahedral Mn is frustrated...



- Magnetic Space Group (Shubnikov) I2'/m (nonconventional of C2'/m).
- Only one magnetic moment to refine (corresponding to Mn in pyramid) in any orientation in the x-y plane.
- No moment on Mn in octahedral site.





 $(La_{0.2}Sr_{0.8})_5Mn_5O_{13}$  vs.  $Sr_5Mn_5O_{13}$  at 10 K



#### **Reminder:** Selective doping in $(La_xSr_{1-x})_5Mn_5O_{13}$ , x=0.0-0.3



Addition of La puts extra electrons on octahedral site.
 Mn1 evolves from 4+ (x=0) to 2.5+ (x=0.3).
 > (La<sub>0.2</sub>Sr<sub>0.8</sub>)<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub> shows elongated octahedra (consistent with Mn<sup>3+</sup>) in the xy plane, but the orientation of the long Mn-O bond is disordered.
 14/May/2012



## Magnetic ordering in (La<sub>0.2</sub>Sr<sub>0.8</sub>)<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub>

- With an elongated Mn<sup>3+</sup> octahedron in the plane the four interactions with neighbouring pyramids are conherent among each-other producing a single spin direction on each site.
- The disorder of the long Mn-O bond in the xy plane produces the moments on Mn1 to be disordered in the long range.



## Magnetic ordering in (La<sub>0.2</sub>Sr<sub>0.8</sub>)<sub>5</sub>Mn<sub>5</sub>O<sub>13</sub>



## Magnetic ordering in $(La_{0.2}Sr_{0.8})_5Mn_5O_{13}$

The disorder of the long Mn-O bond is not perfectly random, the average nuclear structure is not tetragonal but monoclinic therefore in each region of the crystal there is an imbalance between the two orientations of the elongated octahedra. The average magnetic structure shows a value of μ<sub>Mn1</sub> different than zero and smaller than μ<sub>Mn2</sub> because the resulting moment is the average over the two opposite orientations with one of them over-represented respect to the other one.



The magnetic peaks in  $(La_{0.2}Sr_{0.8})_5Mn_5O_{13}$  are broader than in  $Sr_5Mn_5O_{13}$  due to the smaller domain size caused by disorder in the orientation of long Mn-O bond



#### **PERSPECTIVES:**

### The challenge of Sr<sub>7</sub>Mn<sub>7</sub>O<sub>19</sub>...



 $Sr_7Mn_7O_{19}$  phase coexists with  $Sr_5Mn_5O_{13}$  or with an unknown phase for the available samples... solving the magnetic structure using G-K rules has not been fruitful yet...

#### Conclusions

- The "simple" SrMnOy system (2.25<y<3) shows at least 8 different phases at different values of y and synthesis conditions, four of them showing ordered vacancies, two of them stoichiometric and other three showing disordered vacancies.
- HRTEM and ED studies recently performed suggest that additional oxygen ordered vacancies may exist at apparently disordered composition.
- A rich variety of magnetic phases accompany the different structural arrangements where superexchange, double exchange and direct exchange interactions can be found.
- Magnetic frustration in a local and average scale can be found in some phases, but more research is needed to fully determine the magnetic structures in the system.



## Contributions to this work (past and current)

- James D. Jorgensen (RIP), Bogdan Dabrowski, Omar Chmaissem (Argonne Natl. Lab., Mat. Sci. Div. NXRSG)
- Jim Mais, Steve Remsen, Stan Kolesnik (Phisics Dept., Northern Illinois University)
- Simine Short, Joe Fieramosca, Ryoji Kiyanagi (SEPD-Staff), Evan R. Maxey, Jim Richardson Jr. (RIP) (GPPD-Staff at former Argonne's Intense Pulsed Neutron Source).
- Yang Ren (11 ID-C), Brian H. Toby (11BM-B at Argonne's Advanced Photon Source)
- Jun Wang (11BM-B at Argonne's Advanced Photon Source, currently at NSLS-BNL)
- Eduardo Granado, Fabio Furlán Ferreira, Fabiano Yokaichiya (D10B-XPD beamline at Laboratorio Nacional de Luz Síncrotron)
- Joke Haderman (at EMAT-Universiteit Antwerpen)
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14/May/2012

• Thanks to Gabriel Cuello for the invitation.

Mercí beaucoup de votre aimable attention

#### 14/May/2012

All vacancy ordered phases oxidate to cubic SrMnO<sub>3</sub> starting at about 100 °C with full transformation achieved at 200 °C. This is the process used to obtain stoichiometric SrMnO from Ar-annealed SrMnO<sub>v</sub> sample.



Initial SrMnO<sub>2.5</sub> phase heated in-situ in the plate furnace at LNLS.

All vacancy ordered phases oxidate to cubic SrMnO<sub>3</sub> starting at about 100 °C with full transformation achieved at 200 °C. This is the process used to obtain stoichiometric SrMnO from Ar-annealed SrMnO<sub>v</sub> sample.



At 100 °C there are clear evidences of the oxidation of the phase observed by marked peak broadening.

All vacancy ordered phases oxidate to cubic SrMnO<sub>3</sub> starting at about 100 °C with full transformation achieved at 200 °C. This is the process used to obtain stoichiometric SrMnO from Ar-annealed SrMnO<sub>v</sub> sample.



At 200 °C the satellite peaks (caused by vacancy ordering) have disappeared and the main peak shifted to the right, indicating that the unit cell is decreasing due to the addition of oxygen.

All vacancy ordered phases oxidate to cubic SrMnO<sub>3</sub> starting at about 100 °C with full transformation achieved at 200 °C. This is the process used to obtain stoichiometric SrMnO from Ar-annealed SrMnO<sub>v</sub> sample.



At 300 °C (blue) the peak shifts to the left indicating thermal expansion but the shape is constant indicating that the oxidation process is finished. At 500 °C (red) some indication of the formation of hexagonal α phase become evident.

All vacancy ordered phases oxidate to cubic SrMnO<sub>3</sub> starting at about 100 °C with full transformation achieved at 200 °C. This is the process used to obtain stoichiometric SrMnO from Ar-annealed SrMnO<sub>v</sub> sample.



Above 550 °C the α phase (4layer Hexagonal) SrMnO<sub>3</sub> is formed and the perovskite phase disappears almost completely at 600 °C (black)

# A-site size and charge effect on the stability of $A_{4+n}B_{4+n}O_{10+3n}$ compounds

- Vacancy formation transforms two Mn<sup>4+</sup> octahedra into two base-facing Mn<sup>3+</sup> elongated pyramids tightly bound to the vacant site.
- Vacancy ordering requires that distortions associated with orbital and charge ordering of Mn<sup>3+</sup>/Mn<sup>4+</sup> polyhedra form a periodical arrangement.
- The A sub-lattice also shows distortions associated with the reduction of electrostatic shielding between neighbouring A cations around vacancies.
- The degree of network distortion is closely related to the number and relative positioning of vacancies. The larger the number of vacancies the larger the distortion.



# A-site size and charge effect on the stability of $A_{4+n}B_{4+n}O_{10+3n}$ compounds

 $\langle A-A \rangle_{xy}$  is the average distance among A cations in the channels.  $\langle A-A \rangle_z$ : the average A-A distance in two consecutive 001 planes (equals the *c*-axis length). Percentage variation E (%) of  $\langle A-A \rangle_{xy}$  with respect to  $\langle A-A \rangle_z$  in each compound are given as a measure of the deformation of the network.

Compound	Space group	$\langle A - A \rangle_{xy}$	$\langle A\!-\!A\rangle_z$	E(%)	Reference
n = 0		$\sim$			
Ca <sub>4</sub> Mn <sub>4</sub> O <sub>10</sub>	Pbam	4.314	3.735	15.5	Poeppelmeier et al. (1982)
Sr <sub>4</sub> Mn <sub>4</sub> O <sub>10</sub>	Pbam	4.309	3.807	13.2	Suescun et al. (2007)
Sr <sub>4</sub> Cu <sub>4</sub> O <sub>10</sub>	Pbam	4.170	3.731	11.8	Chen et al. (1996)
La4Cu4O10	Pbam	4.526	3.880	16.6	La Placa et al. (1993)
La <sub>4</sub> Cu <sub>4</sub> O <sub>10</sub>	Pbam	4.520	3.880	16.5	Khasanova et al. (1996)
La4Cu4O10	Pbam	4.535	3.880	16.9	Hiroi (1996)
Nd <sub>4</sub> Cu <sub>4</sub> O <sub>10</sub>	Pbam	4.664	3.806	22.5	Chen et al. (1995)
n = 1					
Sr5Mn5O13	P4/m	4.228	3.810	11.0	Suescun et al. (2007)
La5Cu5O13	P2/m	4.556	3.831	18.9	la Placa et al. (1995)
Nd <sub>5</sub> Cu <sub>5</sub> O <sub>13</sub>	P2/m	4.588	3.777	21.5	Chen et al. (1995)
<i>n</i> = 3					
Sr-Mn-O10	P2/m	4.151	3.808	9.0	Suescun et al. (2007)

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

# $A_{4+n}B_{4+n}O_{10+3n}$ compounds in the CaMnO<sub>x</sub> system



Lattice parameters **a** and **b** of observed CaMnO<sub>2.75</sub> compound (Reller et al, 1984; Chiang & Poeppelmeier, 1991) coincide with predicted lattice parameters **a** and **b** of n=4 (pooppoop) hypothetical compound  $A_8B_8O_{22}$  (ABO<sub>2.75</sub>). Observed **c** axis is doubled.

Observed lattice constants of  $CaMnO_{2.667}$  (Reller et al, 1984) coincide with predicted lattice for hypothetical compound n=2 (poppop)  $A_6B_6O_{16}$ .



# $A_{4+n}B_{4+n}O_{10+3n}$ compounds in the CaMnO<sub>x</sub> system



\* Chiang & Poeppelm ier, 1991, Materials Letters....



- Extension of building-block description to include asymmetric blocks allows to generate increasing number of potential structures in the system. None observed so far.
- Two of the models proposed for CaMnO<sub>2.75</sub> (Ching & Poeppelmeier; 1991) can be obtained using n=4 asymmetric blocks with lattice parameters consistent with observed ones.