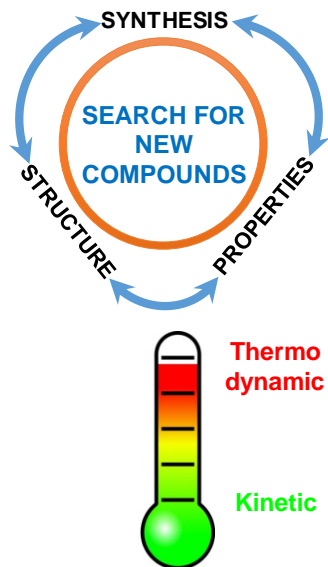


Towards Metastable Compounds by topochemical reactions



Semicond. Sci. Technol. **29** (2014) 064010 (8pp)

Topochemical reactions of layered transition-metal oxides

M A Hayward

Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, UK

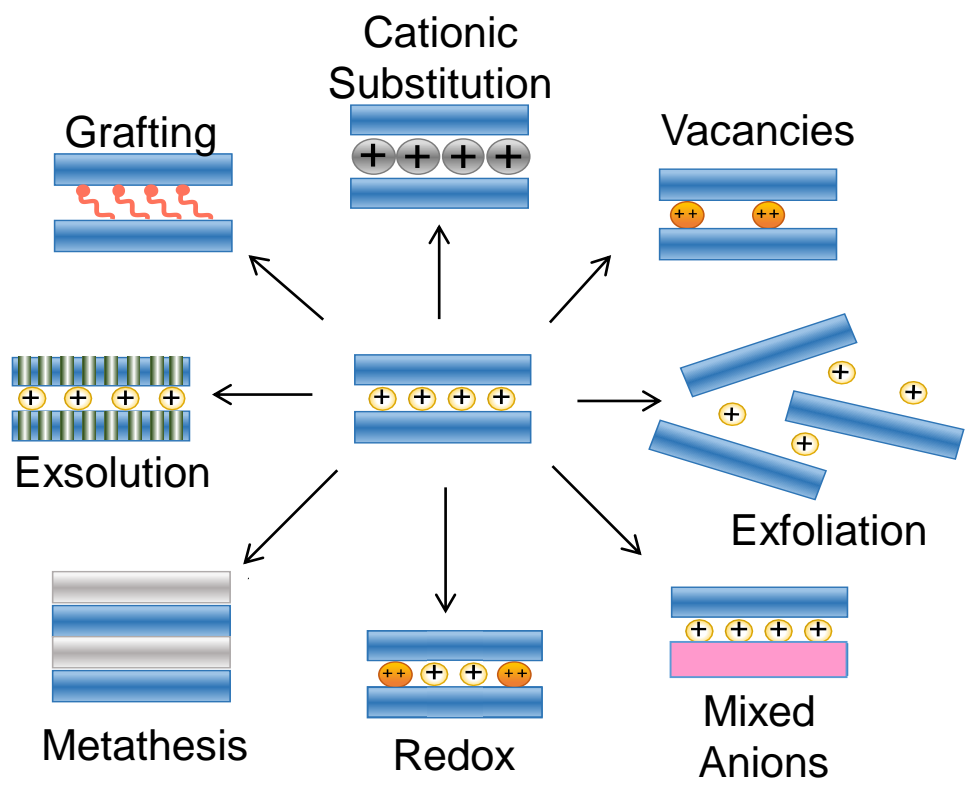
Introduction

The synthesis of complex metal oxides is typically achieved via ‘ceramic’ reactions in which mixtures of binary metal oxides or oxo-acids are reacted at high temperature ($T > 900$ °C). These elevated synthesis temperatures are required because there are large energetic barriers opposing the diffusion of species in the solid state. These barriers to diffusion are generally so large that mass transport makes a dominant contribution to the activation energy of reactions between solid reagents. Given that the motion and diffusion of chemical species is a common feature of all solid–solid reactions, it follows that the activation energies of competing solid–solid reactions tend to be comparable. Thus, at the high temperatures required to overcome these large activation energies, the products of a large number of competing reactions are energetically accessible and in equilibrium with each other, resulting in the formation of the most thermodynamically stable phase or mixture of phases. As a result, high-temperature synthesis routes operate under ‘thermodynamic control’ and are restricted to forming only the most thermodynamically stable phase or mixture of phases for a given composition, precluding the formation of a large number of metastable materials.

phases by exerting some ‘kinetic’ control over the selection of product phases. Under kinetic control the product is the phase which forms fastest rather than the phase which is most thermodynamically stable. Kinetic control can be exerted in solid state reactions by utilizing the different rates of solid-state diffusion of different species, as these correspond to differences in reactivity. For example, in many complex oxides one class of ions, be it a cation (e.g. Li^+ , Na^+ etc) or an anion (O^{2-} , F^- etc), is often considerably more mobile at a given temperature than the surrounding host lattice. As a consequence, these mobile species can be inserted into, or removed from, host phases at low temperature, under conditions in which the surrounding lattice is effectively immobile, to yield metastable phases which are generally inaccessible by high-temperature synthesis routes. Chemical transformations of this type are described as ‘topochemical’ because, unlike the majority of high-temperature reactions, they conserve the basic structural topology of the host material. This retention of structure between reactants and products allows a degree of synthesis planning and product targeting which is generally unavailable in high-temperature syntheses.

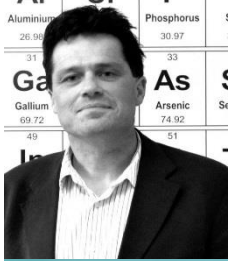
Layered complex oxide phases offer many opportunities for the preparation of new metastable materials by topochemical reaction routes. Layered materials naturally

➤ Topochemical reactions → reduction ... so many
 → reduction using specific hydrides



The Toolbox

Al	Si	P
Aluminium		Phosphorus
26.98		30.97
31		33
Ga		As
Gallium		Arsenic
69.72		74.92
49		51



M. Matthew Rosseinsky
 Liverpool, UK



Hiroshi Kageyama
 Kyoto, Japan



Mike Hayward
 Oxford, UK



Hideo Hosono
 Tokyo, Japan

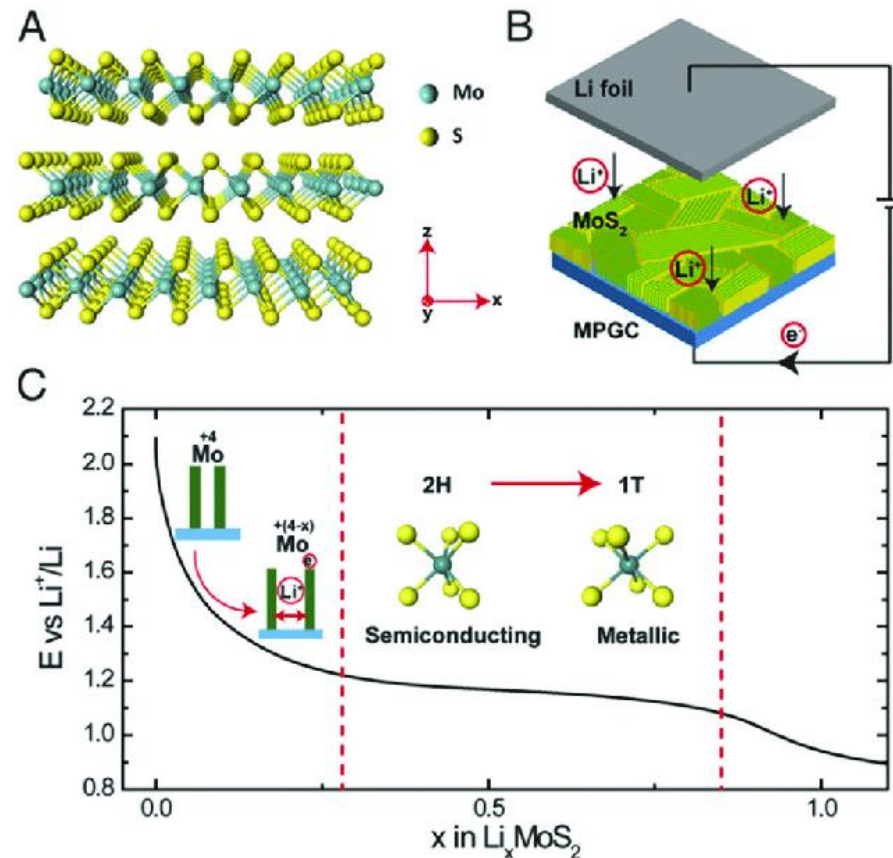
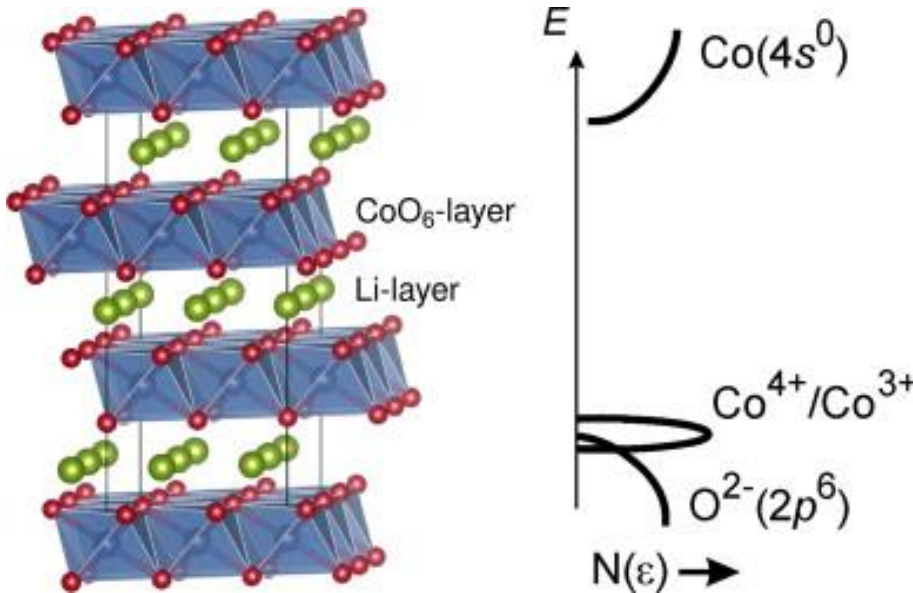
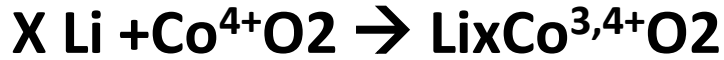
Outline :

- **1-What possible Topochemical reductions ?**
- **2-Reduction by solid Hydrids.**
- **3-What samples (powder, single crystal , films...).**
- **4-Some “Local” results on “funny” square-planar Nickelates.**

1-Electrochemical intercalation

Topochemical reduction vs. oxidation inseparable chemistry

by reversibility

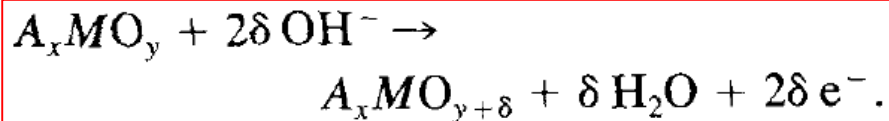


J.B. Goodenough Chemistry
Nobel Prize 2019

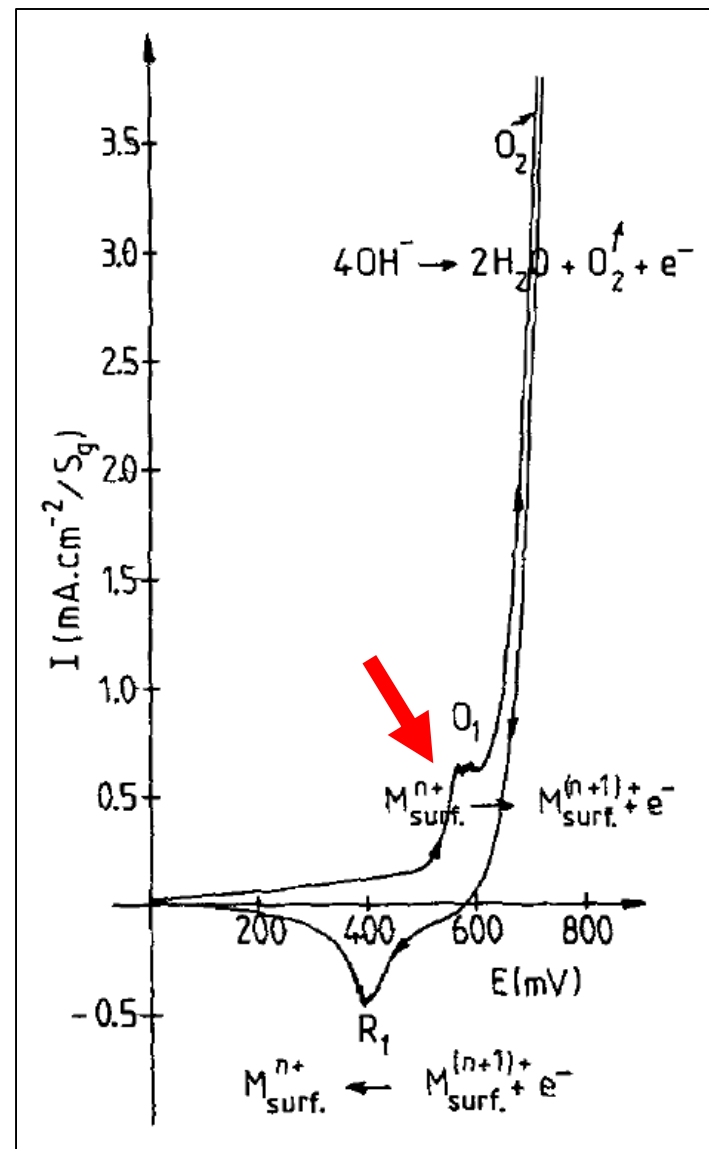
1-Electrochem. oxygen (de)intercalation

... a question of Electrochemistry ...

3 electrodes Electrochemistry : the material is the working electrode : Electrolysis of water (OH⁻)



ICMCB. JSSC 96, 20, (1992)

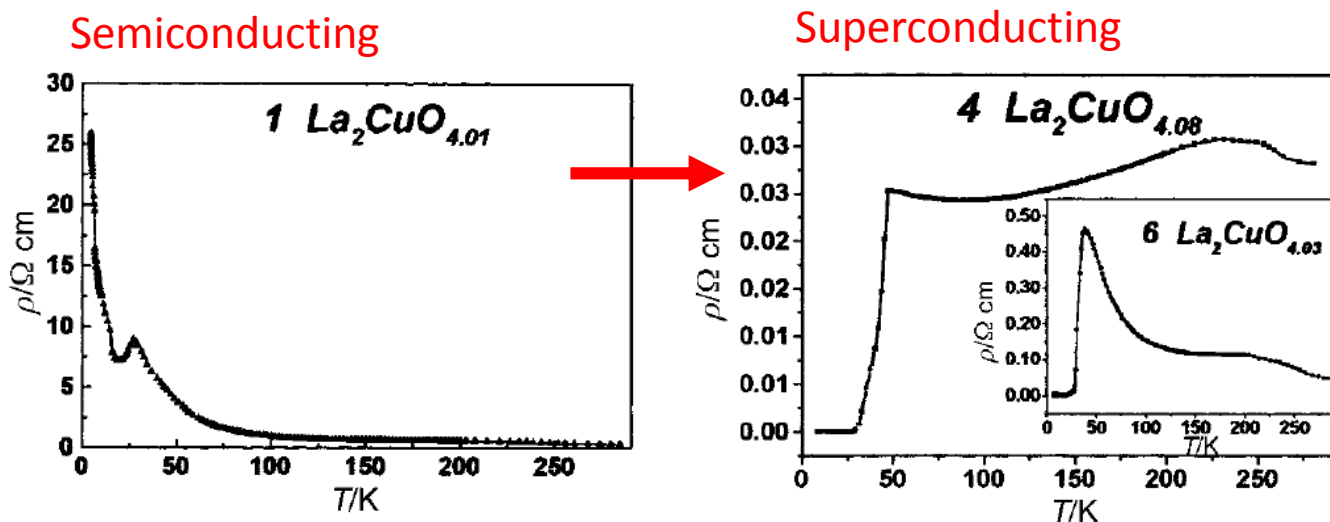


1-Electrochem. oxygen (de)intercalation

... a question of Electrochemistry ... Improvement

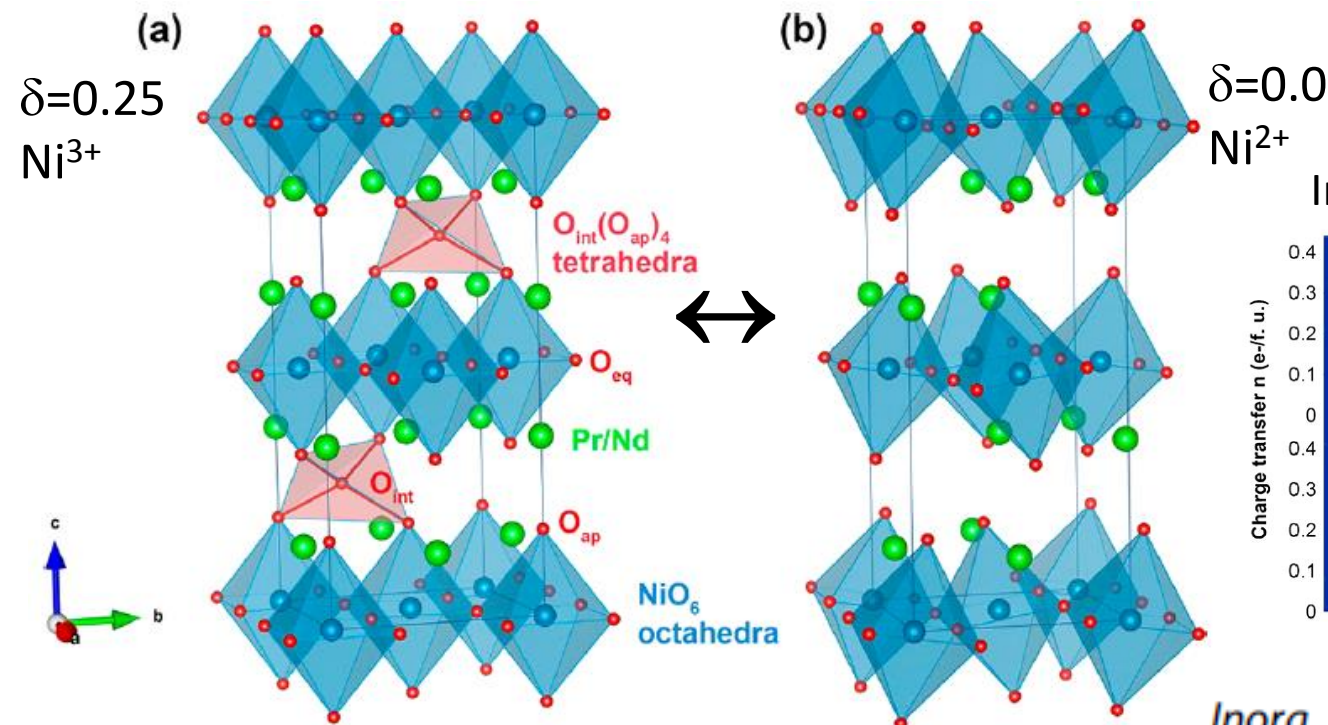
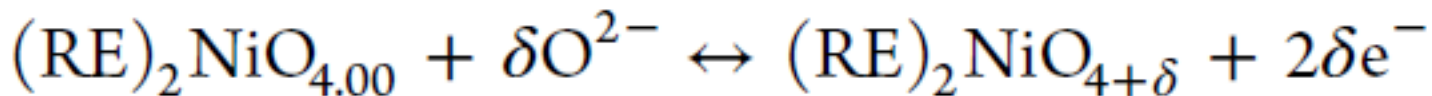
The electrochemical intercalation of oxygen into La_2CuO_4 has been carried out for the first time in anhydrous organic±inorganic media such as dimethyl sulfoxide (DMSO)/0.1M NaClO_4 or $n\text{Bu}_4\text{NBF}_4$. The electrochemical reaction needs the presence of an oxygen source (KO_2) even with potential oxidizing supporting electrolytes (NaClO_4). The anodic polarisation is performed at room temperature, with the aim of replacing the aggressive alkaline media.

ICMCB, J. Mater. Chem., 2000, 10, 829

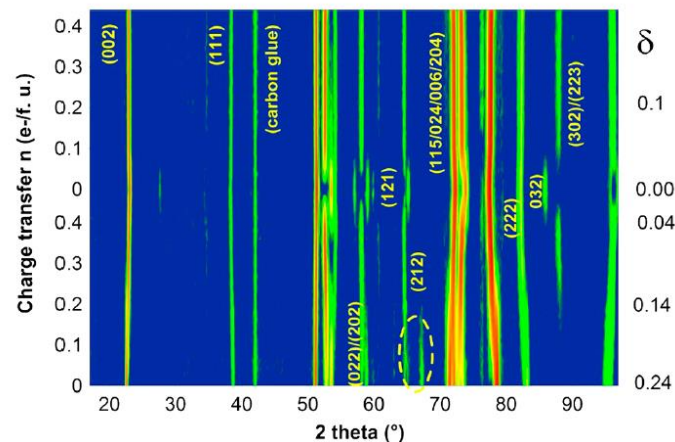


1-Electrochem. oxygen (de)intercalation

Application to Nickelates / Ionic conductivity problematic,
Rennes, Montpellier, Nantes, Bordeaux



In situ, NPD



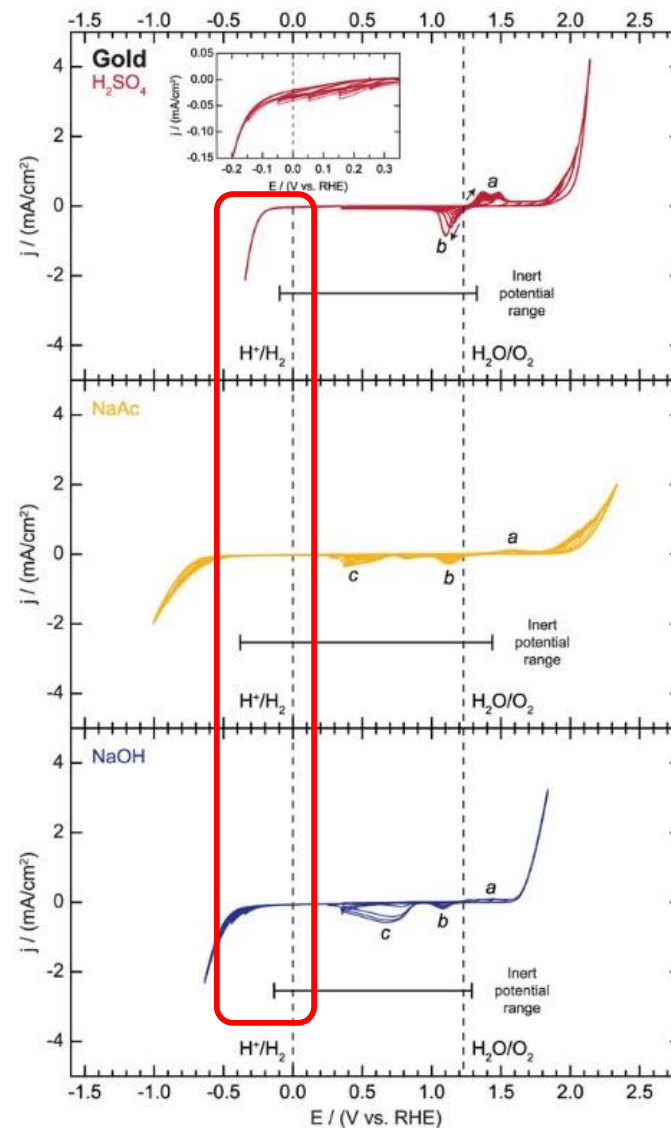
Inorg. Chem. 2018, 57, 4657–4666

1-Electrochem. oxygen (de)intercalation

Topochemical reduction :

Tunable electrochemical “window “

Catal. Lett. (2015) 145: 95



1. Heterogeneous Reduction by H₂ gaz

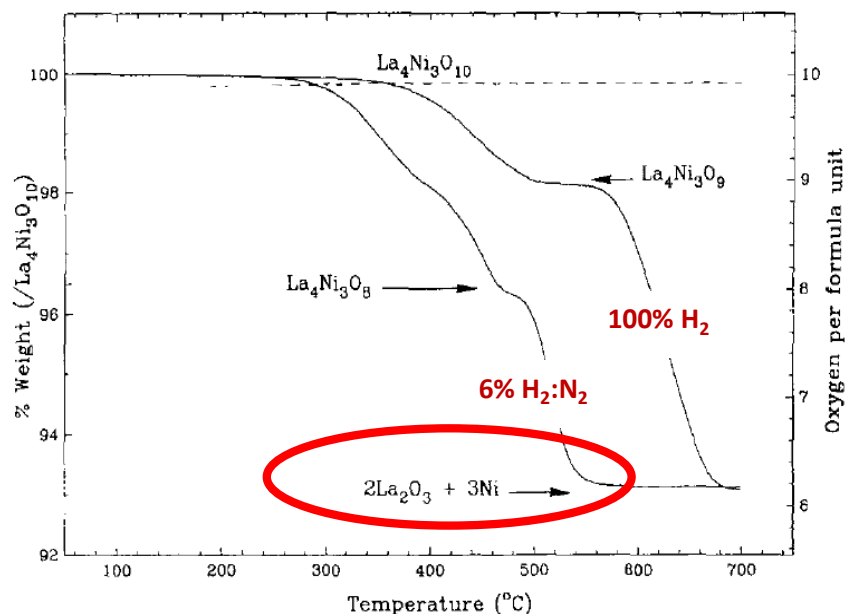
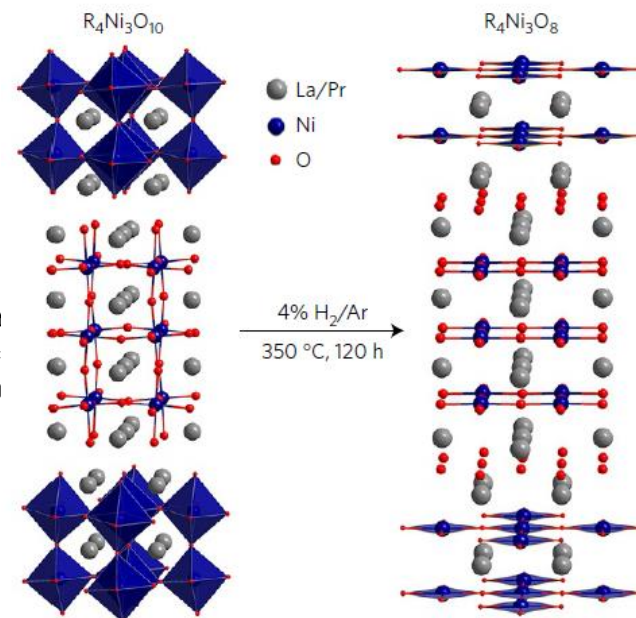


FIG. 2. Thermogravimetric analyses of $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$ ($\delta = 0$ and 2) performed on a Perkin-Elmer System 4 equipment upon heating (heating rate 10°C/min) in the following atmospheres: (a) $\text{La}_4\text{Ni}_3\text{O}_{10}$, under pure hydrogen; (b) $\text{La}_4\text{Ni}_3\text{O}_{10}$, under diluted hydrogen (6% H₂, 94% N₂); (c) $\text{La}_4\text{Ni}_3\text{O}_8$, under oxygen

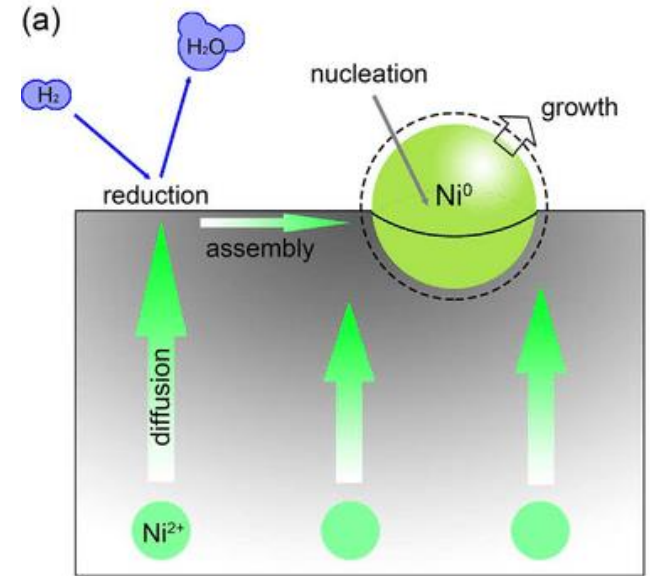
Lacorre, JSSC, 97, 495, 1992



1. Metal Exsolution during reduction

Something to avoid !!!

Rather common : exsolution of Ni^0 from perovskites
 → decoration by nanometric Ni^0 ... catalysis



Nanometric nickel exsolution in the hexagonal perovskite $\text{Ba}_8\text{Ta}_6\text{NiO}_{24}$: Survey of the structural, magnetic and catalytic features

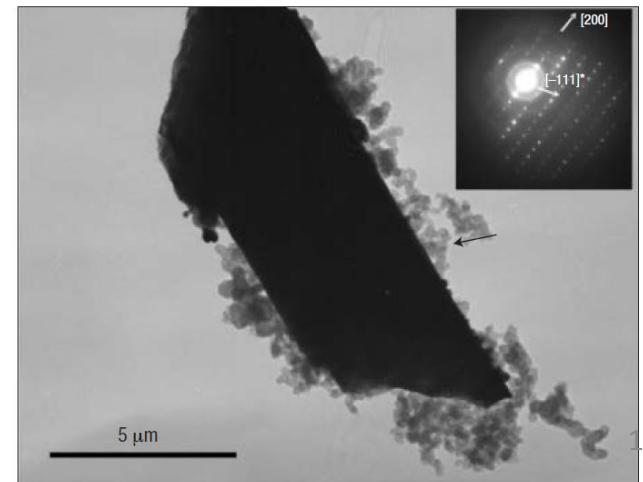
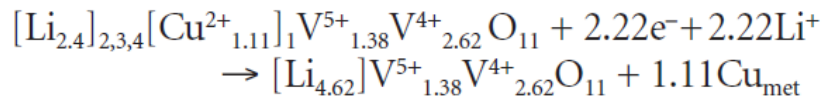
Tanguy Pussacq^a, Olivier Mentré^a, Franck Tessier^b, Axel Löfberg^a, Marielle Huvé^a, Jesús Guerro Caballero^a, Silviu Colis^c, Houria Kabbour^{a,*}

^a Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181, UCSC - Unité de Catalyse et Chimie du Solide, F-59000, Lille, France
^b Institut des Sciences Chimiques de Rennes (UMR CNRS 6226), Verres et Céramiques, Université de Rennes 1, 263 Avenue du Général Leclerc, F-35042, Rennes Cedex, France
^c Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 CNRS, 23 rue du Loess, BP 43, F-67034, Strasbourg Cedex 2, France

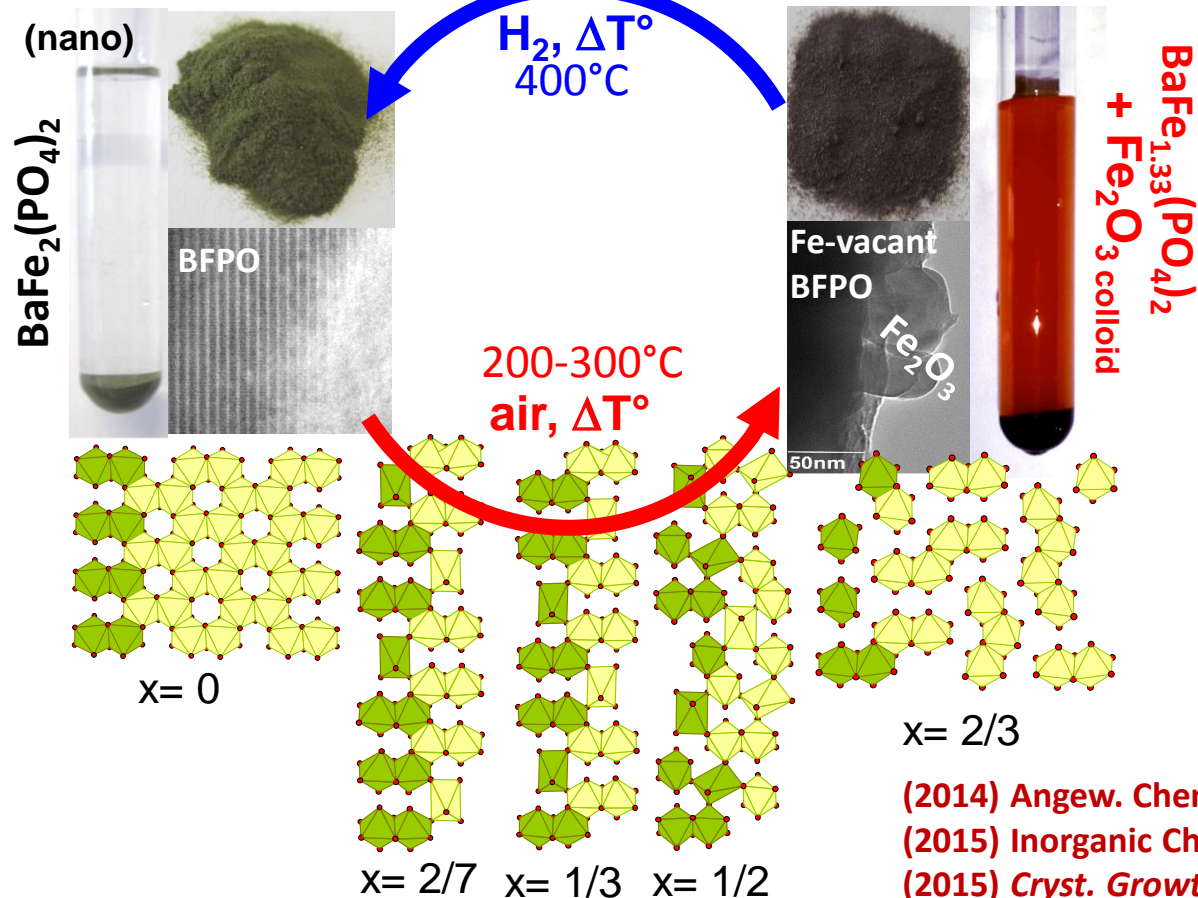
→ nanometric Cu^0 ... during Li intercalation **ARTICLES**

A reversible copper extrusion–insertion electrode for rechargeable Li batteries

M. MORCRETTE¹, P. ROZIER², L. DUPONT¹, E. MUGNIER², L. SANNIER¹, J. GALY² AND J.-M. TARASCON*¹



1. Reversible Metal Exsolution during topochemical red./oxyd.



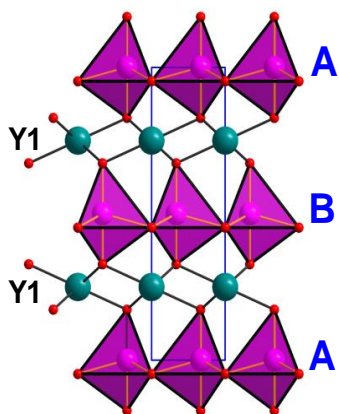
(2014) *Angew. Chem. – Int. Ed.*, 53, 13365

(2015) *Inorganic Chemistry*, 54, 8733

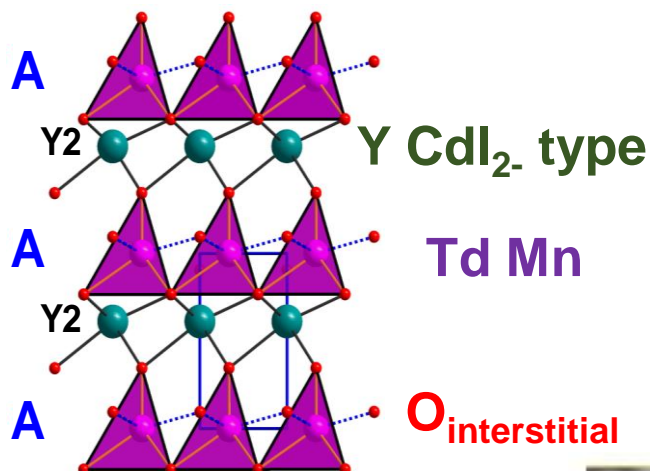
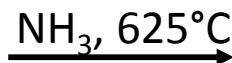
(2015) *Cryst. Growth Des.* 15, 4237

Topochemical Reduction of YMnO_3 into a Composite Structure

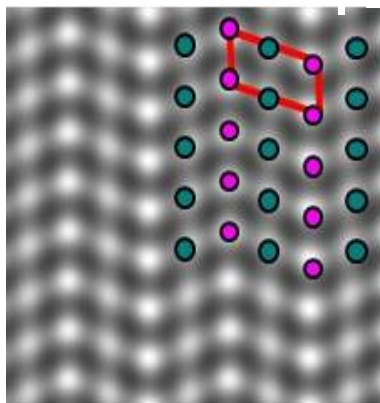
Houria Kabbour,^{*,†} Gilles H. Gauthier,[‡] Franck Tessier,[§] Marielle Huvé,[†] Tanguy Pussacq,[†] Pascal Roussel,[†] Michael A. Hayward,^{||} Zulma L. Moreno B.,[‡] Maya Marinova,[⊥] Marie Colmont,[†] Silviu Colis,[#] and Olivier Mentré[†]



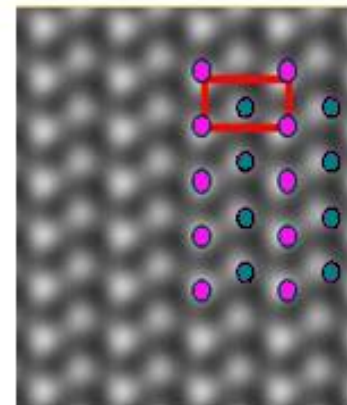
ABA Mn-stacking
« $[\text{YMnO}_{3-x}]$ »



AAA Mn-stacking
« $[\text{YMnO}_{2+x}]$ »



$\text{YMn}^{3+}\text{O}_3$



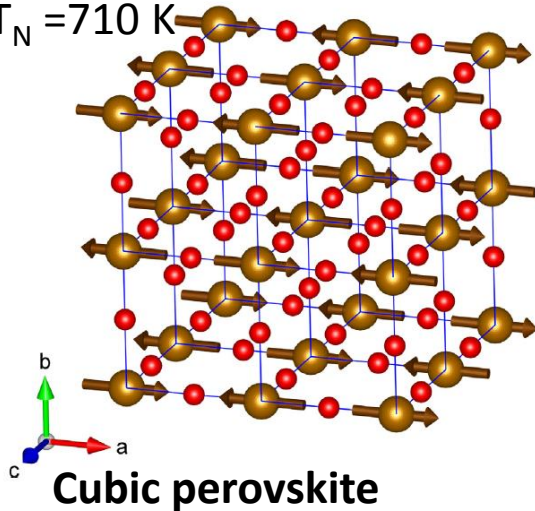
$\text{YMn}^{2+}\text{O}_{2.5}$

1. Topochemical Red. by Fluorination

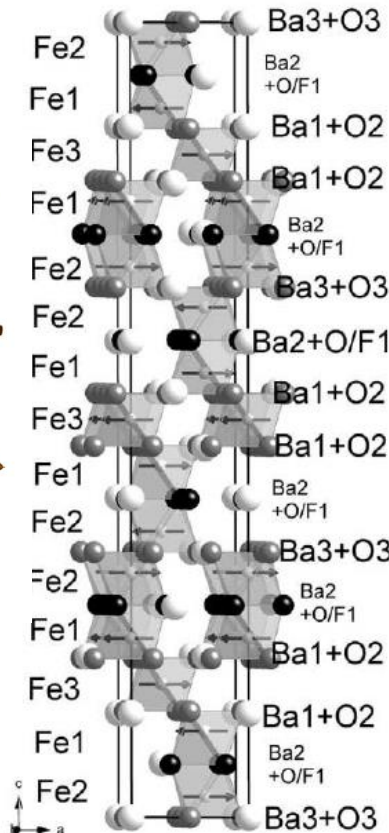
F^- for O^{2-} , many ways (see A. Demourgues) ... a simple one using PVDF

$$AFe^{3/4+}O_{3-d} + PVDF \rightarrow AFe^{3+}O_2F, 300-400^\circ C$$

Robust AFM,
 $T_N = 710\text{ K}$



Hex. perovskite



In contrast, high amounts of fluoride ions cannot usually be stabilised in alkaline earth-containing oxide compounds at high temperatures [22]. This is related to the high stability of the alkaline earth (AE) fluorides AEF_2 . A variety of fluorination agents can be used to modify the anion sublattice and the oxidation state of the transition metal in a preformed oxide, for example CuF_2 [23], F_2 [24] and XeF_2 [25] have all been used for this purpose. In 2002, polyvinylidene fluoride (PVDF) was shown to be a useful fluorination agent [22] and can be used for the synthesis of a variety of iron-containing oxide fluoride perovskite compounds with a high fluorine content, e.g. cubic $BaFeO_2F$ [26,27], $SrFeO_2F$ [28,29], $Sr_xBa_{1-x}FeO_2F$ [30,31], $La_{1-x}SrFeO_{3-x}F_x$ [32,33] and hexagonal $6H-BaFeO_2F$ [34]. The high stability of the Ba/Fe sublattice and nature of PVDF as a low temperature fluorination agent allows the synthesis of different modifications of the metastable compound $BaFeO_2F$. Recently, Anji Reddy and Fichtner [35] showed

Birmingham group, JSSC,184, 2011, 1361.
JSSC,203, 2013, 218 ... etc

Fig. 3. Crystallographic and (excerpt of the) magnetic structure of 15R- $BaFeO_2F$. The F1/O1 anion site (black ions) is occupied by 83.33% of F^- and 16.67% of O^{2-} .

1. Topochemical Red. by Fluorination

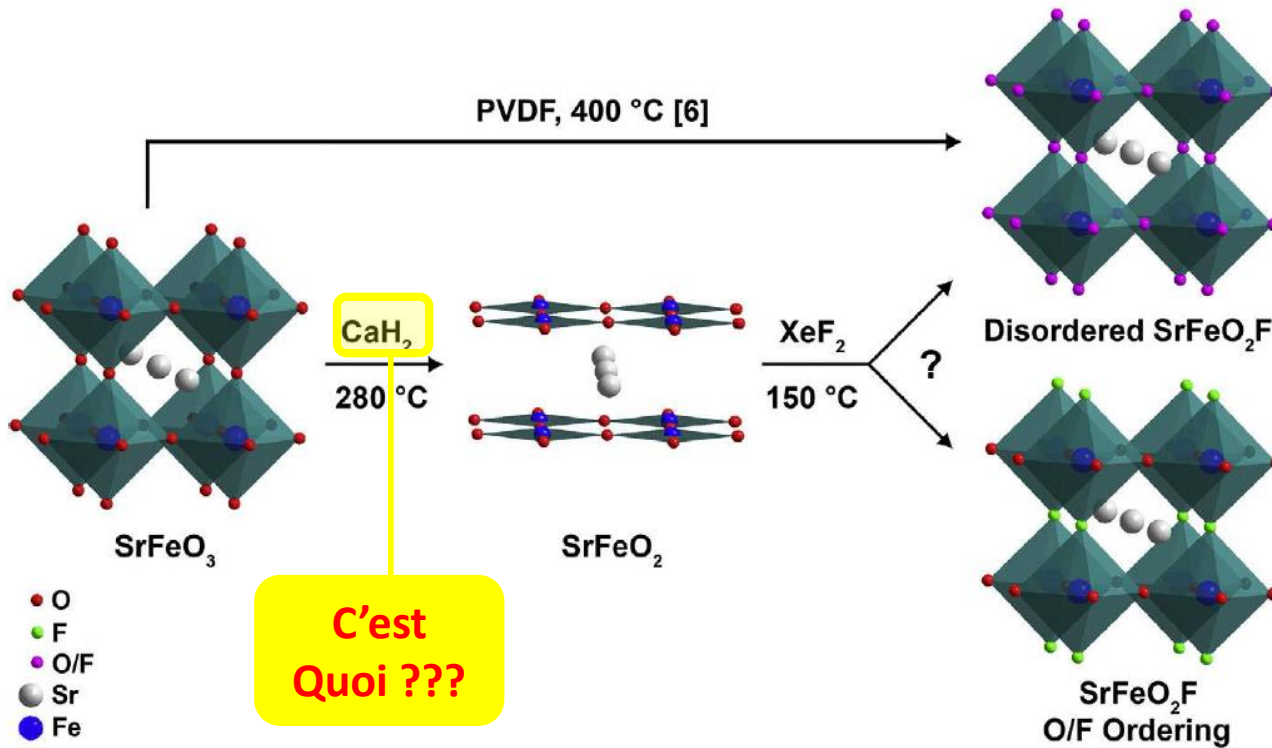


Fig. 1. Multistep synthetic route for the preparation of the SrFeO_2F oxyfluoride.

C.K. Blakely et al. / *Journal of Fluorine Chemistry* 159 (2014) 8–14

1. Topochemical Red. by Fluorination

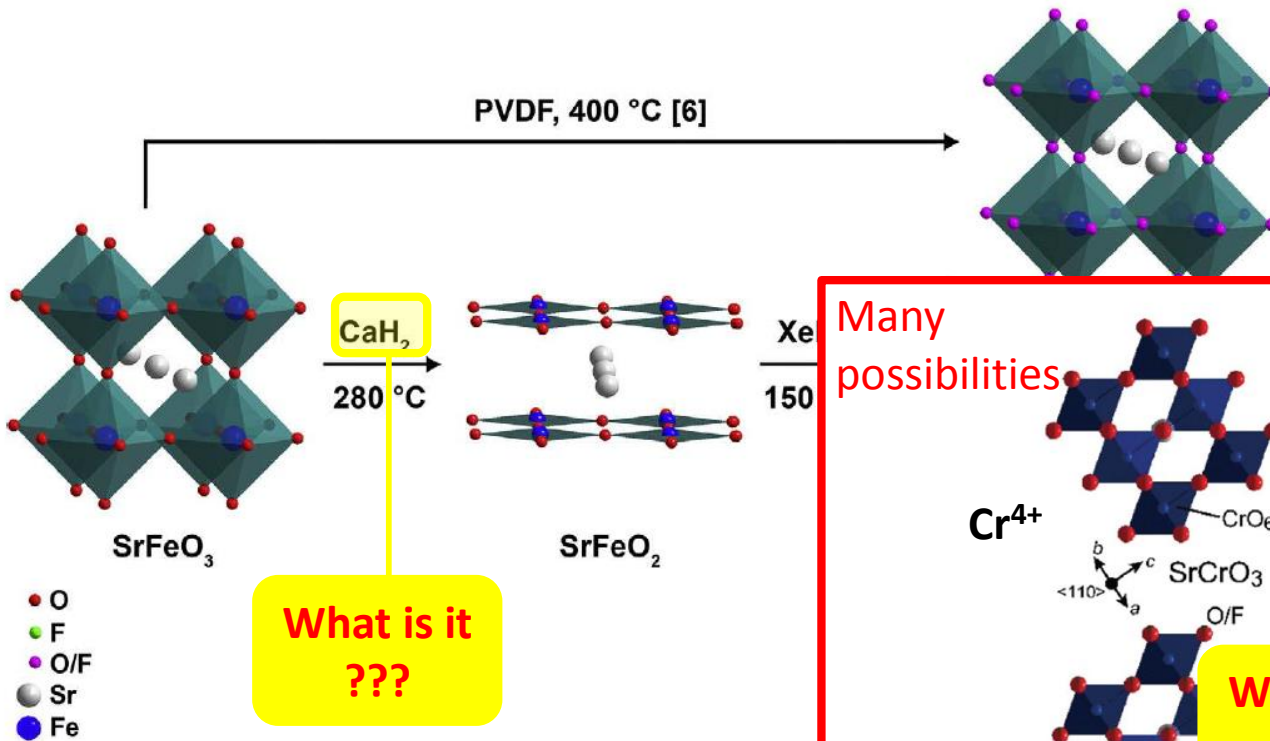


Fig. 1. Multistep synthetic route for the preparation of

C.K. Blakely et al./Journal of Fluorine Chemistry 159 (2014) 8

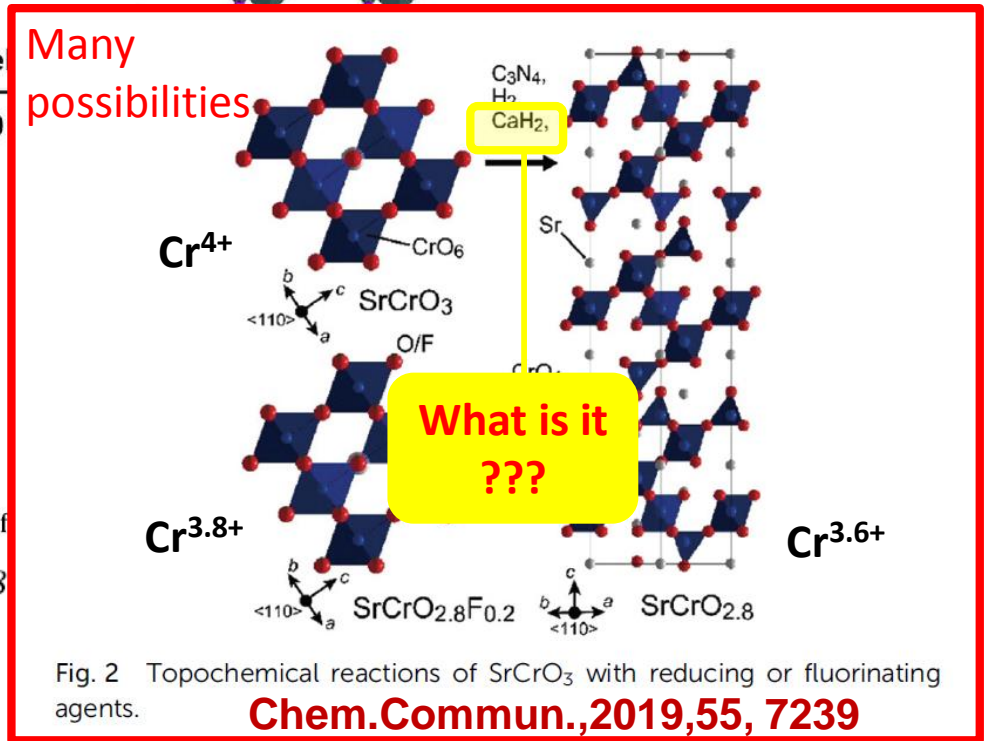


Fig. 2 Topochemical reactions of SrCrO_3 with reducing or fluorinating agents.

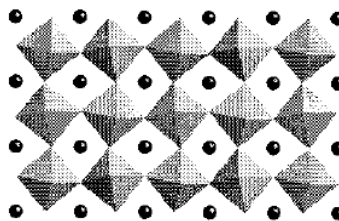
Chem.Comm.,2019,55, 7239

1. Topochemical Red. by solid Hydrids

J. Am. Chem. Soc. **1999**, *121*, 8843–8854

Sodium Hydride as a Powerful Reducing Agent for Topotactic Oxide Deintercalation: Synthesis and Characterization of the Nickel(I) Oxide LaNiO_2

M. A. Hayward, M. A. Green, M. J. Rosseinsky,* and J. Sloan



3+
 $\text{LaNiO}_3 - R\bar{3}c$



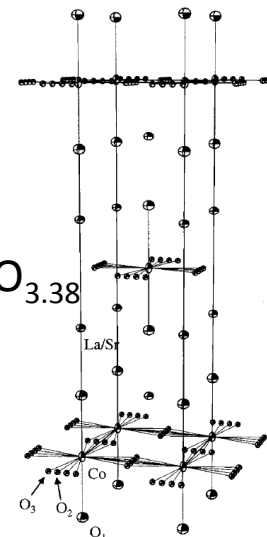
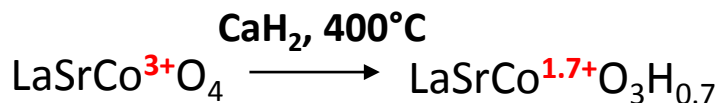
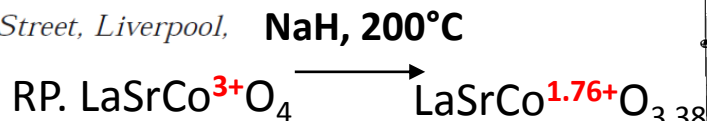
1+
 $\text{LaNiO}_2 - P4/mmm$

Chem. Mater. **2000**, *12*, 2182–2195

Anion Vacancy Distribution and Magnetism in the New Reduced Layered Co(II)/Co(I) Phase $\text{LaSrCoO}_{3.5-x}$

M. A. Hayward and M. J. Rosseinsky*

Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, United Kingdom



Science

The Hydride Anion in an Extended Transition Metal Oxide Array: $\text{LaSrCoO}_3\text{H}_{0.7}$

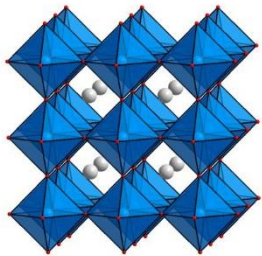
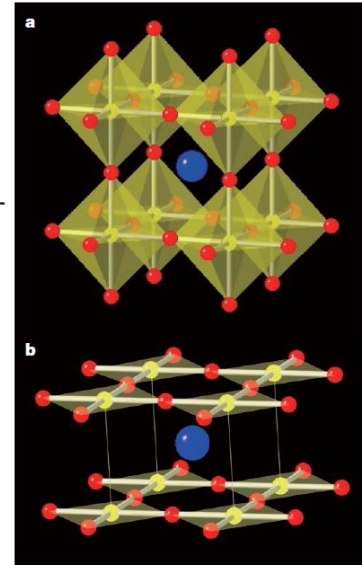
M. A. Hayward, E. J. Cussen, J. B. Claridge, M. Bieringer, M. J. Rosseinsky, C. J. Kiely, S. J. Blundell, I. M. Marshall and F. L. Pratt

LETTERS

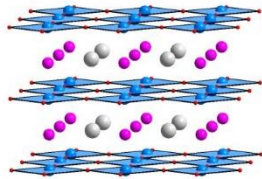
→ Reduction

Infinite-layer iron oxide with a square-planar coordination

Y. Tsujimoto¹, C. Tassel^{1,2}, N. Hayashi³, T. Watanabe¹, H. Kageyama¹, M. Mizuno¹, M. Takano^{4,5}, M. Ceretti², C. Ritter⁶ & W. Paulus²

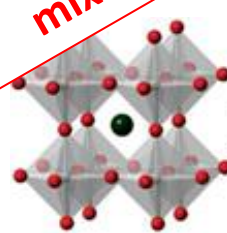
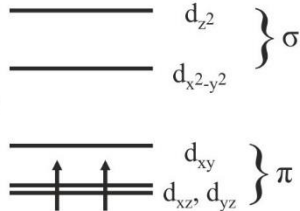
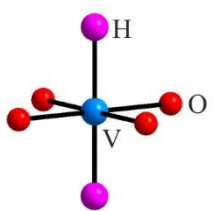


SrVO₃

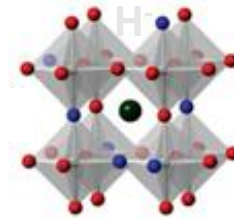


SrVO₂H

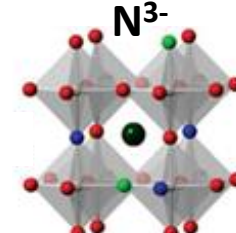
→ Oxyhydrides, mixed anions ...



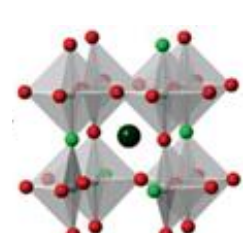
BaTiO₃



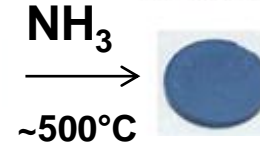
BaTiO_{3-x}H_x



BaTiO_{3-x}H₂N_y



BaTiO_{3-x}N_{2x/3}

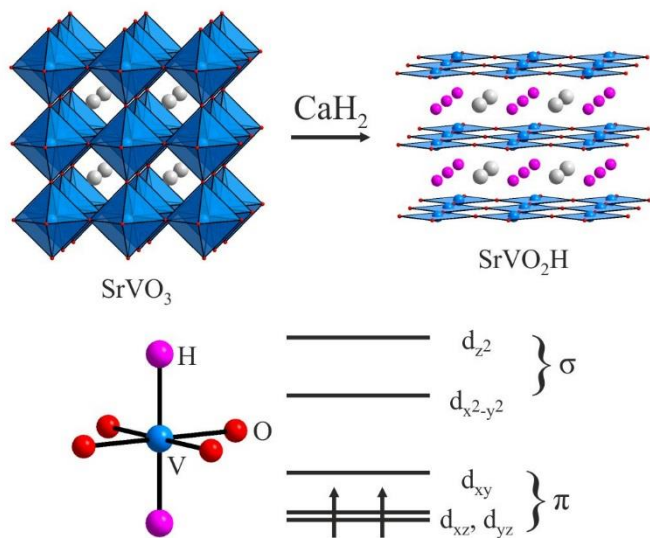


Angewandte Chemie, 53 (2014) 7556.

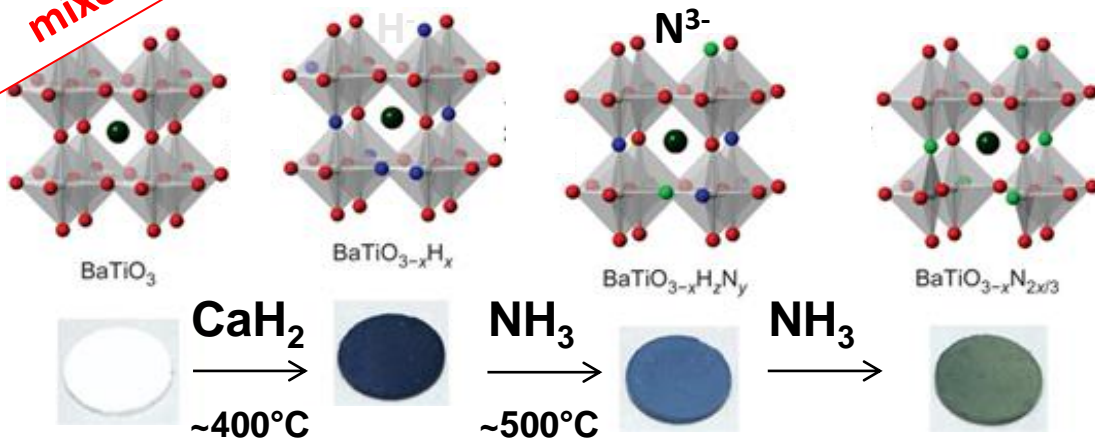
Yajima et al., Nature Chem. 2015

2. Reactivity with solid Hydrides

Interest: Binary metal hydrides can be utilized to extract oxide ions from complex transition metal oxides. The resulting phases **can contain transition metal cations in highly unusual oxidation states** and/or coordination environments. Alternatively binary hydrides can also bring about **hydride-for-oxide anion exchange to yield oxide-hydrides** phases, which contain both O^{2-} and H^- anions. **The lack of π -symmetry valence orbitals on the hydride ion** means that anion-ordered oxide hydride phases can have electronic band structures which are **qualitatively different from their all-oxide analogues**.



→ Oxyhydrides, mixed anions ...



Angewandte Chemie, **53** (2014) 7556.

Yajima et al., Nature Chem. 2015

2. Hydrides: Experimental ... crucial T° choice

280°C

METHODS SUMMARY SrFeO₂

The reduction of SrFeO_{2.875} was performed using CaH₂ as a reducing agent, as described for LaSrCoO₄ (ref. 3). SrFeO_{2.875} and a two-molar excess of CaH₂ were finely ground in an Ar-filled glove box, sealed in an evacuated Pyrex tube, and reacted at 553 K for two days. The residual CaH₂ and the CaO byproduct were removed from the final reaction phase by washing them out with a NH₄Cl/methanol solution. Chemical analyses were based on EDS and thermogravi-

Reduction of SrVO₃ → SrVO₂H

Small-scale test reactions showed no reaction occurred between SrVO₃ and CaH₂ at temperatures below 600 °C. Reactions between SrVO₃ and CaH₂ performed at temperatures between 600 °C and 630 °C yielded a new phase that could be indexed on the basis of a tetragonal unit cell with lattice parameters $a = 3.934(1) \text{ \AA}$ and $c = 3.667(1) \text{ \AA}$ as determined by X-ray powder diffraction data. Reactions performed above 630 °C led to sample decomposition

600-630°C

2. Beware of the Oxy-Hydrids NdNiO_xH_y

LETTER

<https://doi.org/10.1038/s41586-01>

Superconductivity in an infinite-layer nickelate

Danfeng Li^{1,2*}, Kyuho Lee^{1,3}, Bai Yang Wang^{1,3}, Motoki Osada^{1,4}, Samuel Crossley^{1,2}, Hye Ryoung Lee^{1,4}, Yi Cui^{1,4}, Yasuyuki Hikita¹ & Harold Y. Hwang^{1,2*}

Sr ion. We note, however, that the metallic nature of $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ counteracts these trends. No signature of a fluorite defect phase²⁰ was observed in asymmetric θ - 2θ XRD scans of our samples (both doped

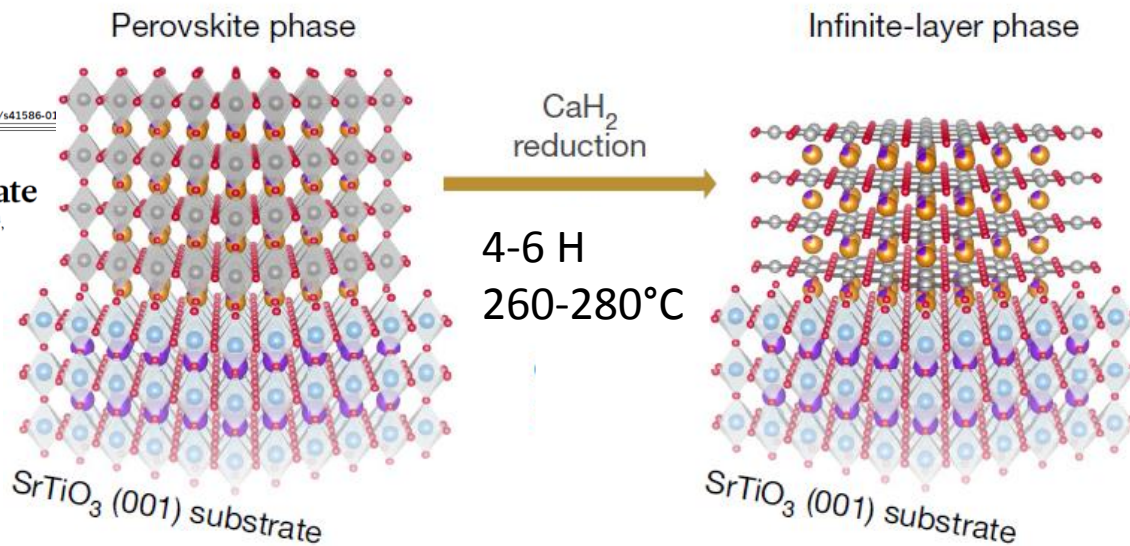
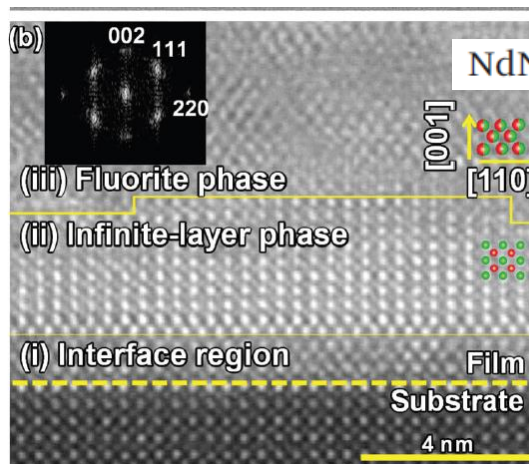


Fig. 1 | Topotactic reduction of nickelate thin films. Schematic crystal

Formation of defect-fluorite structured NdNiO_xH_y epitaxial thin films via a soft chemical route from NdNiO_3 precursors

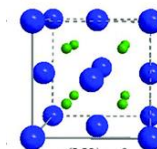
T. Onozuka,^a A. Chikamatsu,^{*a} T. Katayama,^a T. Fukumura^b and T. Hasegawa^{a,c}

240-400°C



NdNiO_xH_y with $(x, y) \approx (2.3, 0.7)$

Fluorite-type



NdNiO_2

SrTiO_3 (001)

2. Hydrid: Experimental ... crucial T° choice

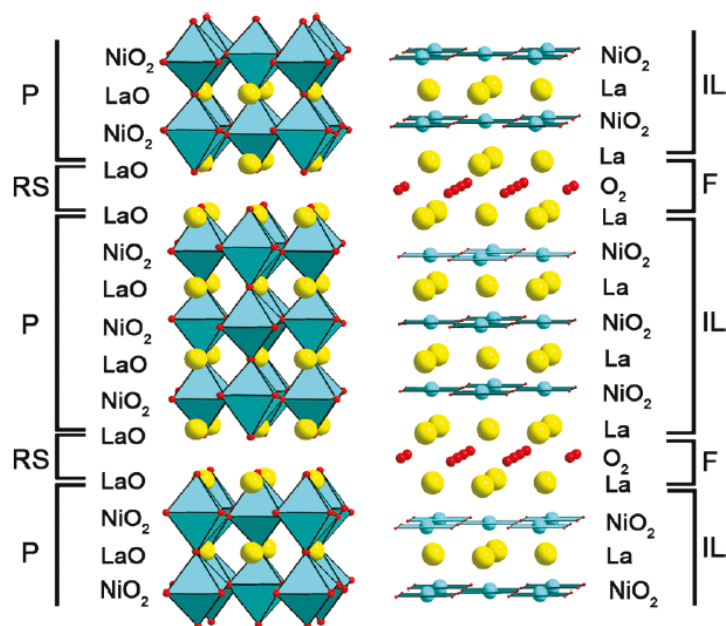


Figure 1. Structure models of $\text{La}_4\text{Ni}_3\text{O}_{10}$ (left) and $\text{La}_4\text{Ni}_3\text{O}_8$ (right) with denoted layers and structural blocks: P, perovskite; RS, rock salt; IL, infinite layer; F, fluorite. Yellow, cyan, and red balls represent La, Ni, and O atoms, respectively.

$\text{La}_4\text{Ni}_3\text{O}_8$ was also obtained as a main phase by the solvothermal reduction with NaH in pentane at 150 °C. The solubility of both NaH and NaOH is expected to be much lower in nonpolar solvents like pentane than in the polar glyme ethers; therefore, the reducing power of NaH in pentane cannot be attributed to reagent/product solubility.

Solvent

Table 1. Products of $\text{La}_4\text{Ni}_3\text{O}_{10}$ Reduction by Different Techniques

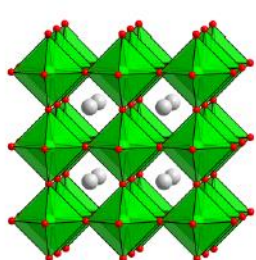
reagent/solvent	reaction temperature (reaction time), autogenous pressure for solvothermal condition	relative content (%) of $\text{La}_4\text{Ni}_3\text{O}_{10}/\text{La}_4\text{Ni}_3\text{O}_9/\text{La}_4\text{Ni}_3\text{O}_8$ (normalized to 100% total)
H_2	300 °C (100 h)	0/0/100
	250 °C (120–360 h)	0/100/0
	200 °C (360 h)	no reaction
NaH	200 °C (240 h)	0/30/70
	150 °C (240 h)	no reaction
NaH/triglyme	200 °C (168 h)	0/100/0
	150 °C (120 h)	10/90/0
NaH/diglyme	200 °C (168 h), 2.9 atm	0/30/70
	150 °C (240 h)	0/90/10
NaH/pentane	200 °C (240 h), 59.7 atm	0/0/100
	150 °C (72 h), 15.7 atm	0/25/75

reductive power of the proposed solvothermal method. Introduction of pressure is favorable and leads to formation of pure $\text{La}_4\text{Ni}_3\text{O}_8$ at lower temperatures than previously reported. Experiments are underway to investigate whether new metastable complex oxides can be synthesized by the proposed method.

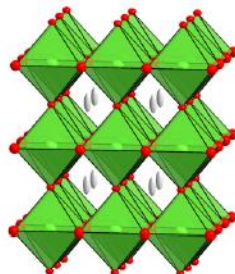
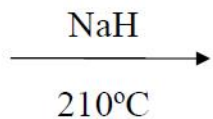
Pressure

Inorg. Chem. 2011, 50, 6696

2. Hydrid, exp. ... What reduc. Agent ?



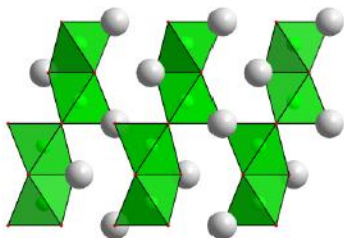
$\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$
($0.6 < x < 1$)



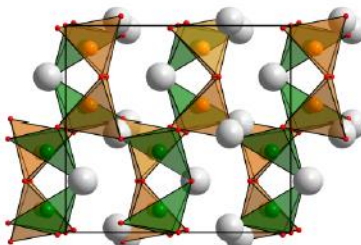
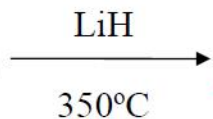
$\text{La}_{1-x}\text{Ca}_x\text{MnO}_2$
($0.6 < x < 1$)
 $\text{Mn}^{1+/2+}$

+ NaOH

J. Am. Chem. Soc., **133** (2011) 18397.



4H-BaMnO_{3-x}



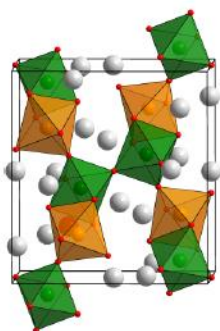
4H-BaMnO_2
 Mn^{2+}

+ Li_2O + H_2

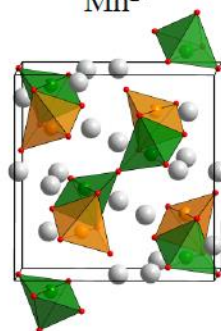
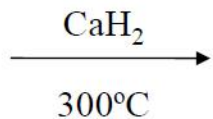


**Can give
oxy-hydrids**

J. Am. Chem. Soc., **131** (2009) 10598.



$\text{Sr}_7\text{Mn}_5\text{O}_{15}$



$\text{Sr}_7\text{Mn}_5\text{O}_{13}$

+ CaO + H_2



**Can give
oxy-hydrids**

Chem. Comm., **2** (2004) 170.
J. Solid State Chem., **180** (2007) 2851.

3. Reduction by Hydrides: What samples ?

Powder: 95% of the papers !!!

→ Topochemical means no fully reconstructive

What about epitaxial films ???

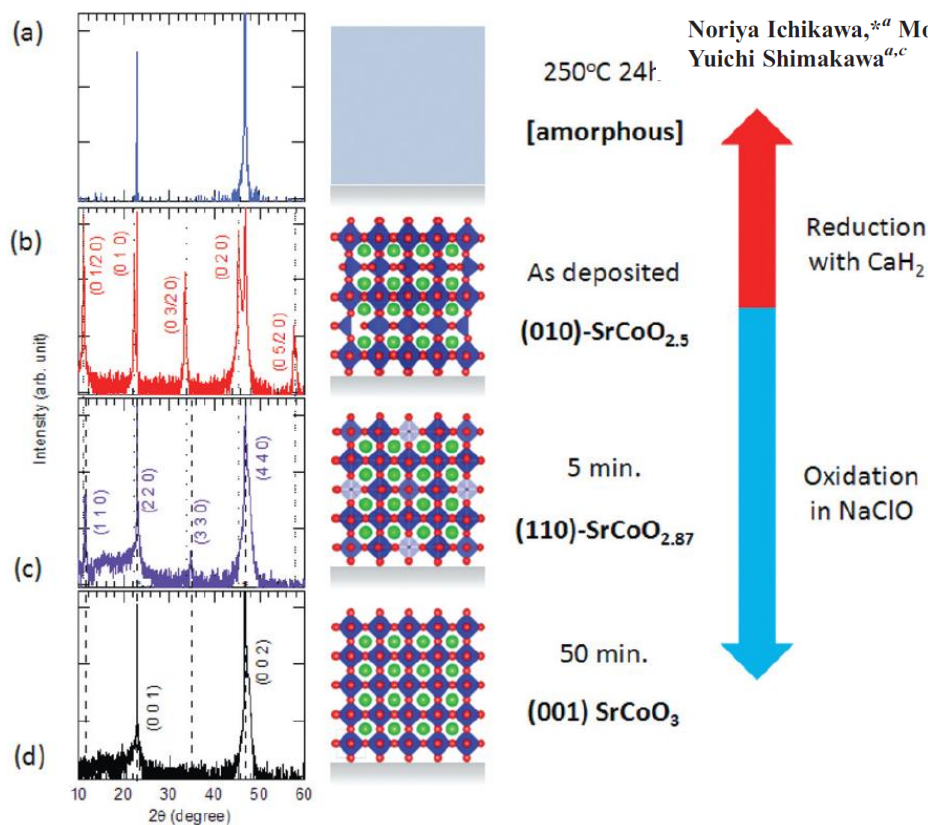
Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 10507

www.rsc.org/dalton

Reduction and oxidation of SrCoO_{2.5} thin films at low temperatures

Noriya Ichikawa,^{a,c} Monika Iwanowska,^{a,b} Masanori Kawai,^a Christophe Calers,^{a,b} Werner Paulus^{b,d} and Yuichi Shimakawa^{a,c}

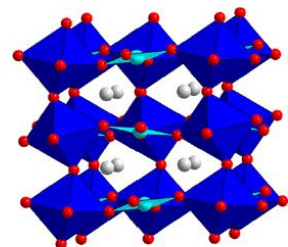


In conclusion, we synthesized (010)-oriented SrCoO_{2.5} brownmillerite thin films on a LSAT (100) substrate, and then attempted topotactic reduction and oxidation at low temperatures. Unlike the iron- or nickel-based perovskite oxides, the brownmillerite SrCoO_{2.5} film reduced at 200 °C by calcium hydride became an amorphous film, indicating that Co²⁺O₄ square planar geometry in the perovskite cation framework is unstable. Room temperature oxidation by NaClO, on the other hand, changed SrCoO_{2.5} into the ferromagnetic and conducting SrCoO₃. The present results offer important information on the stability of the oxidation state and the oxygen coordination of cobalt in oxides, and the information will also be useful for developing solid oxide fuel cells.

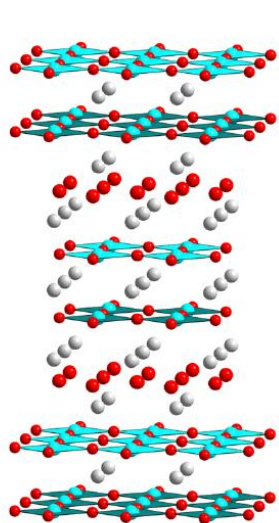
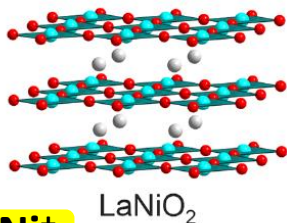
Synthesis and Magnetism of Extended Solids Containing Transition-Metal Cations in Square-Planar, MO_4 Coordination Sites

Michael A. Hayward*[ⓧ]

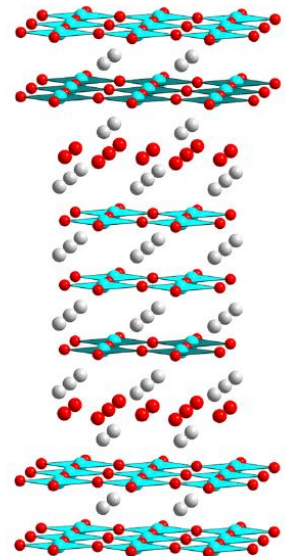
Reduced-Square plane topologies



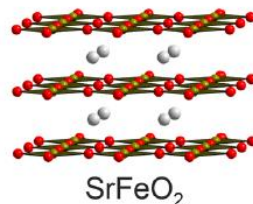
Ni^{2+}/Ni^+



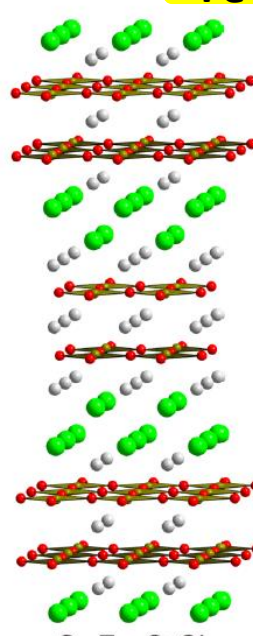
$La_3Ni_2O_6$



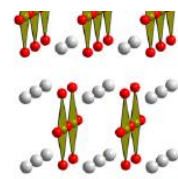
$La_4Ni_3O_8$



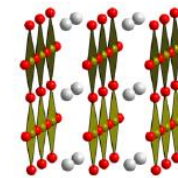
Fe^{2+}



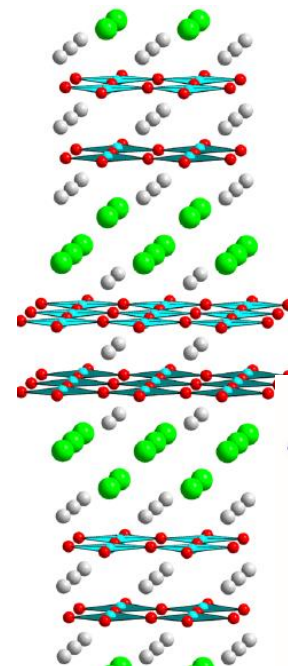
$Sr_3Fe_2O_4Cl_2$



Sr_2FeO_3



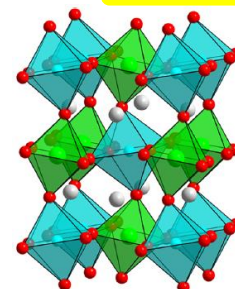
$Sr_3Fe_2O_5$



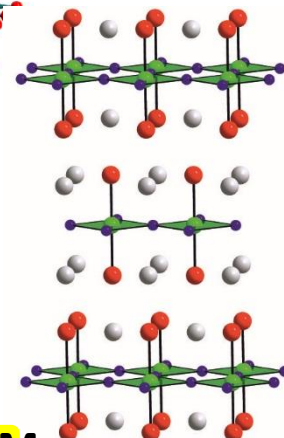
$Sr_3Co_2O_4Cl_2$

Co^{2+}/Co^+

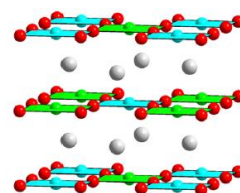
4d-5d TM



$LaSrNiRuO_6$



$LaSr_3NiRuO_4H_4$



$LaSrNiRuO_4$

$S=0 Ru^{2+}, S=1 Ni^+$

Synthesis and Magnetism of Extended Solids Containing Transition-Metal Cations in Square-Planar, MO_4 Coordination Sites

Michael A. Hayward*[✉]

Other Possible Square plane based topologies For reduction

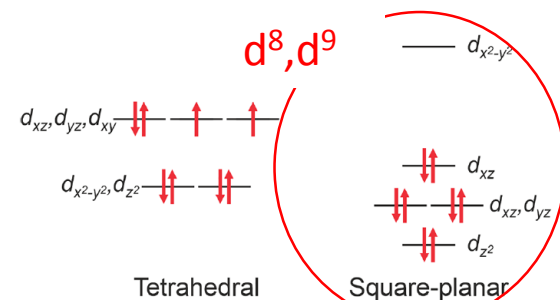
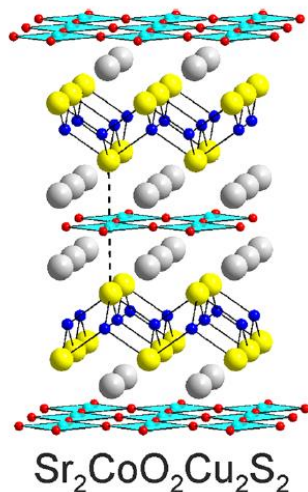
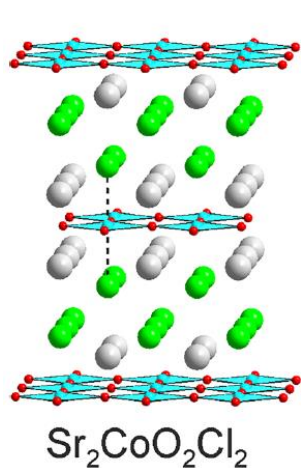
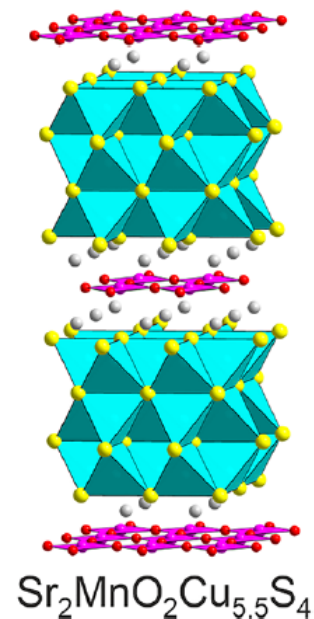
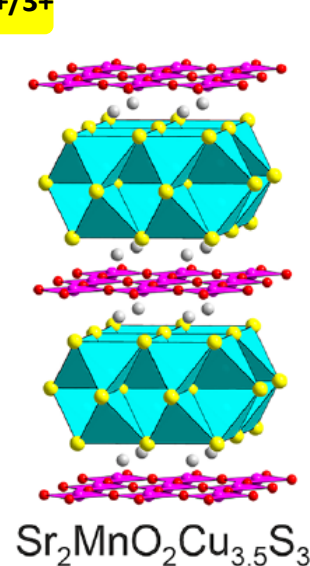
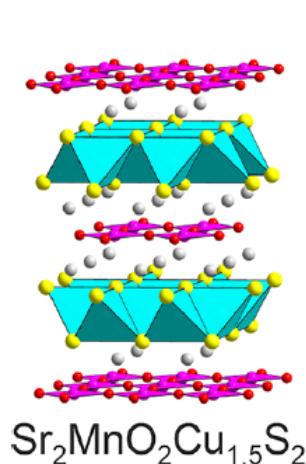


Figure 1. d-orbital splitting of the tetrahedral (T_d) and square-planar (D_{4h})-coordinated MO_4 units, illustrating the potential for enhanced electronic stability of D_{4h} coordination for a d^8 or d^9 electron count.

Co²⁺



Mn^{2+/3+}



3.Reduction by Hydrides: What samples ?

APPLIED PHYSICS LETTERS 92, 161911 (2008)

Single-crystal epitaxial thin films of SrFeO₂ with FeO₂ “infinite layers”

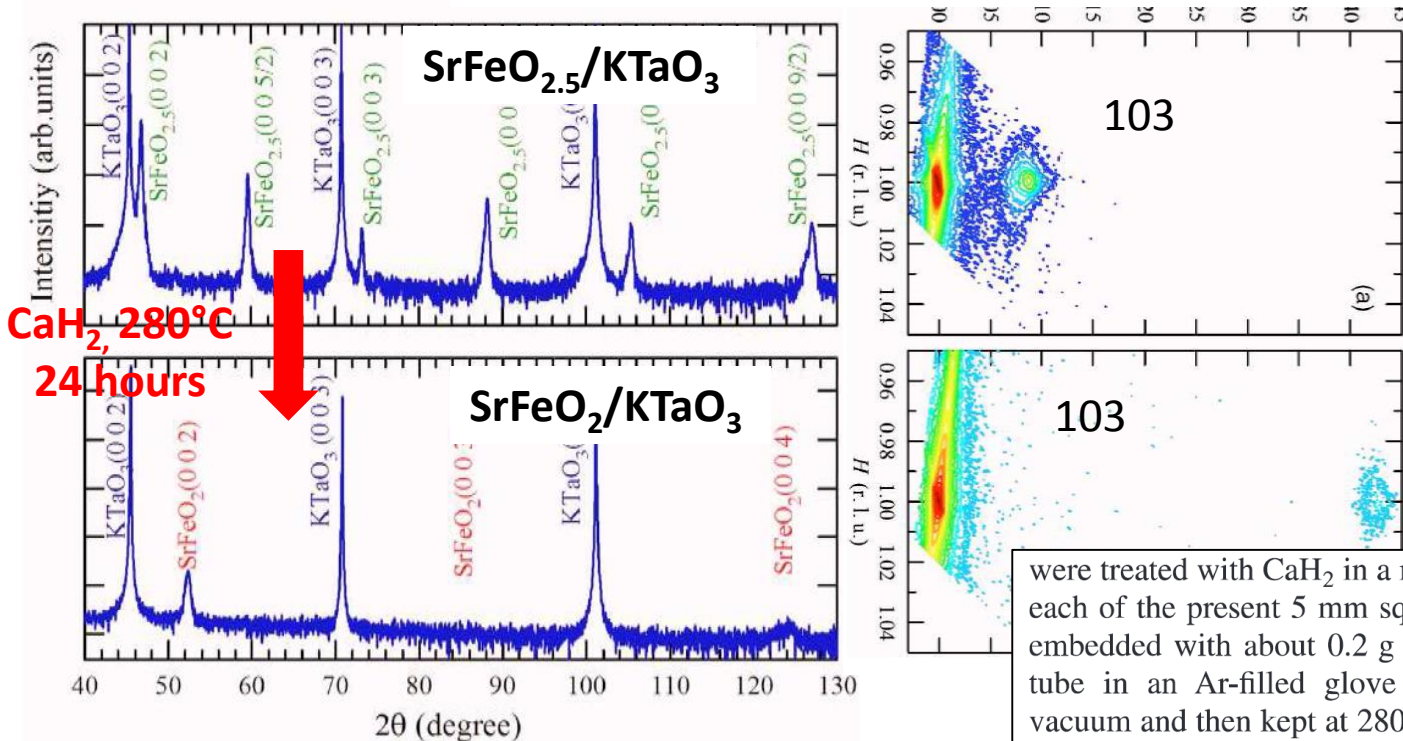
Preserved crystallinity and texture

Satoru Inoue,¹ Masanori Kawai,¹ Yuichi Shimakawa,^{1,a)} Masaichiro Mizumaki,² Naomi Kawamura,² Takashi Watanabe,³ Yoshihiro Tsujimoto,³ Hiroshi Kageyama,³ and Kazuyoshi Yoshimura³

¹Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

²Japan Synchrotron Radiation Research Institute/SPRING-8, Sayo, Hyogo 679-5198, Japan

³Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan



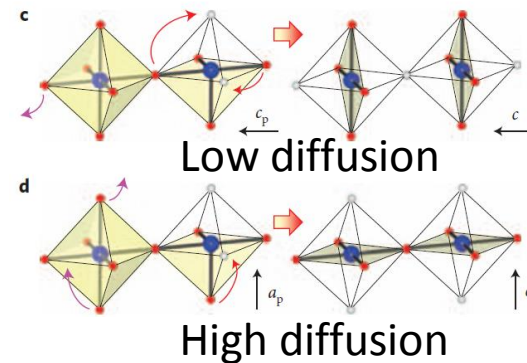
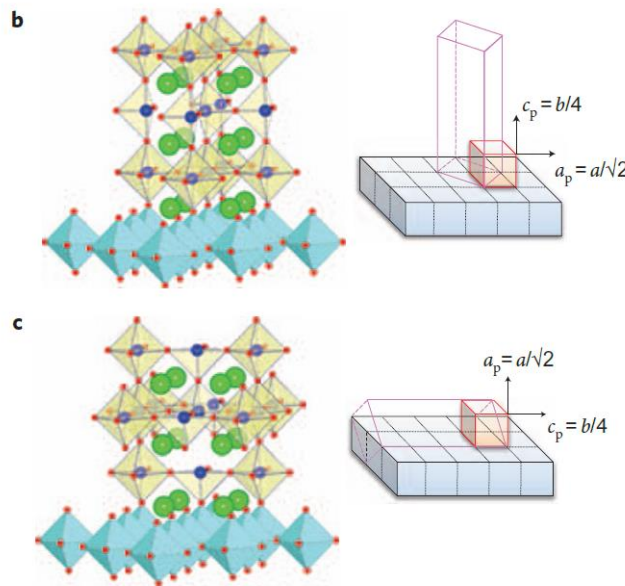
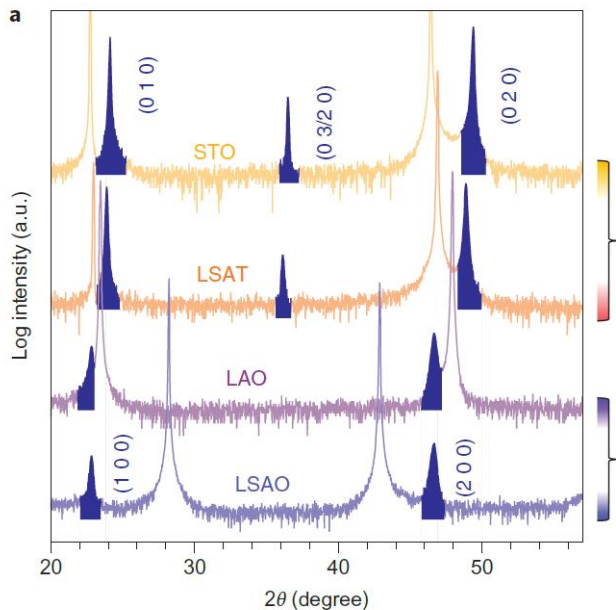
were treated with CaH₂ in a mixed compressed disk, whereas each of the present 5 mm square SrFeO_{2.5} film samples was embedded with about 0.2 g of CaH₂ in an evacuated Pyrex tube in an Ar-filled glove box. The tube was sealed in vacuum and then kept at 280 °C for 24 h. The residual products, including CaH₂, on the film surface were removed by washing with 2-butanone. The crystal structure of the result-

3.Reduction by Hydrids: What samples ?

Specific O²⁻- and □ diffusion paths that guaranty the structural preservation... by reactivity time during CaH₂ reduction.

Anisotropic oxygen diffusion at low temperature in perovskite-structure iron oxides

Satoru Inoue¹, Masanori Kawai¹, Noriya Ichikawa¹, Hiroshi Kageyama², Werner Paulus³ and Yuichi Shimakawa^{1*}



3. Reduction by Hydrids: What samples ?

Single Crystals : YES, possible ... but small and twinned

OPEN ACCESS
IOP Publishing

Journal of Physics D: Applied Physics
doi:10.1088/0022-3727/48/50/504004

Solid-state reactivity explored *in situ* by synchrotron radiation on single crystals: from SrFeO_{2.5} to SrFeO₃ via electrochemical oxygen intercalation*

A Maity¹, R Dutta^{1,2}, B Penkala¹, M Ceretti¹, A Letrouit-Lebranchu¹, D Chernyshov³, A Perichon¹, A Piovano⁴, A Bossak⁵, M Meven⁶ and W Paulus¹

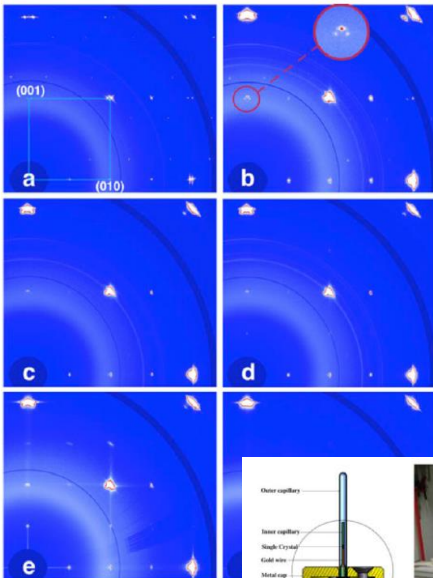
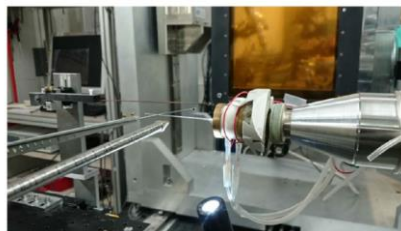


Figure 8. Evolution of the (0kl) plane oxygen intercalation in SrFeO_{2.5} (a) v framework up to the cubic SrFeO₃ pe



nature
physics

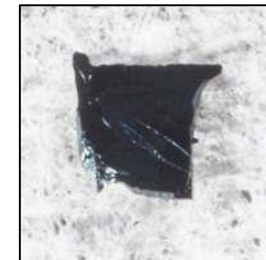
ARTICLES

PUBLISHED ONLINE: 12 JUNE 2017 | DOI: 10.1038/NPHYS4149

Large orbital polarization in a metallic square-planar nickelate

Junjie Zhang^{1*}, A. S. Botana¹, J. W. Freeland², D. Phelan¹, Hong Zheng¹, V. Pardo^{3,4}, M. R. Norman¹ and J. F. Mitchell¹

Single crystals of La438 and Pr438 were prepared by reducing their parent $n = 3$ Ruddlesden–Popper (R–P) compounds, R₄Ni₃O₁₀ (R = La, Pr, hereafter R4310, see Fig. 1a and Supplementary Fig. 1). To our knowledge, this is the first report of single-crystal growth of Pr4310 and Pr438 (see Supplementary Tables 1 and 2 for structural details of Pr438). The valence of Ni in R438 and R4310 is consistent with the expected values 1.33+ and 2.67+, respectively, as measured by Ni L edge spectroscopy (see Supplementary Fig. 2 and Supplementary Section 3, X-ray absorption spectroscopy (XAS)).



Absorption coefficient	31.210 mm ⁻¹
F(000)	768
Crystal size	0.061 × 0.041 × 0.039 mm ³
θ range for data collection	3.197 to 31.278°
Reflections collected/Independent	2584/242 [$R_{int} = 0.0260$]
Completeness to θ = 14.357°	98.6%

4. Some “Local” results on square-planar “exotic” Nickelates



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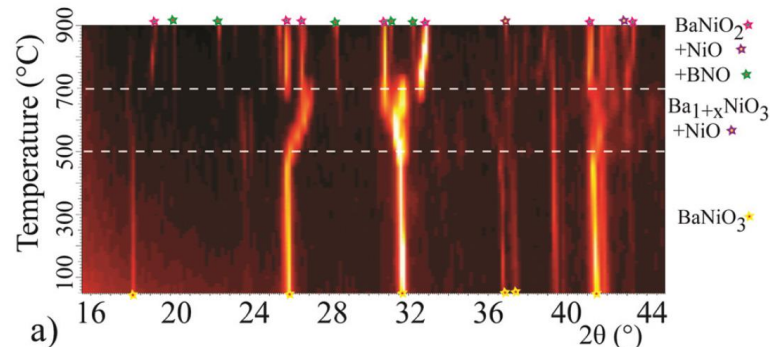
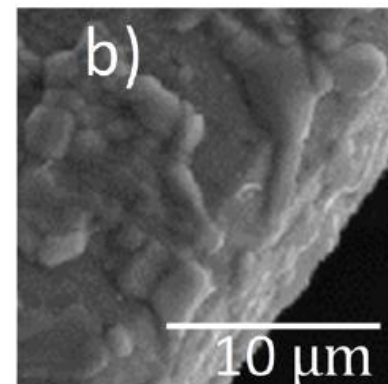
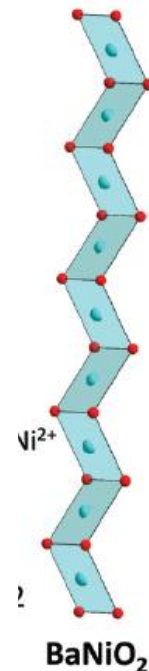
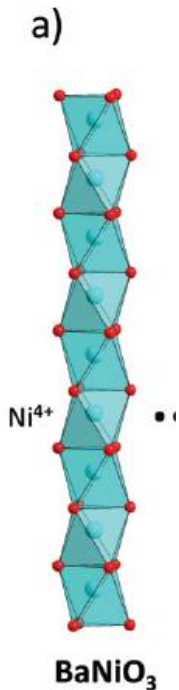
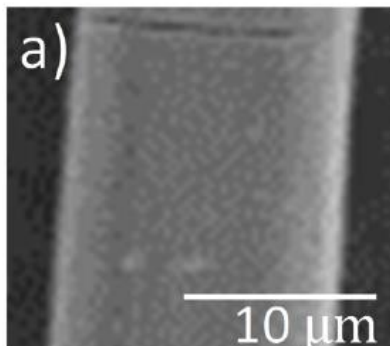
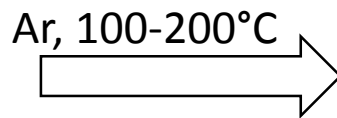
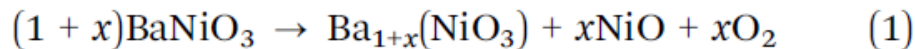
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Cite this: *Chem. Commun.*, 2019, 55, 3717

Received 3rd December 2018,
Accepted 4th March 2019

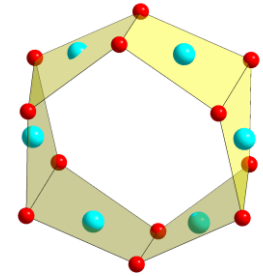
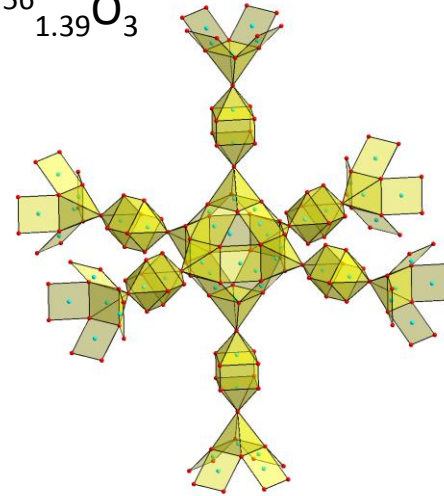
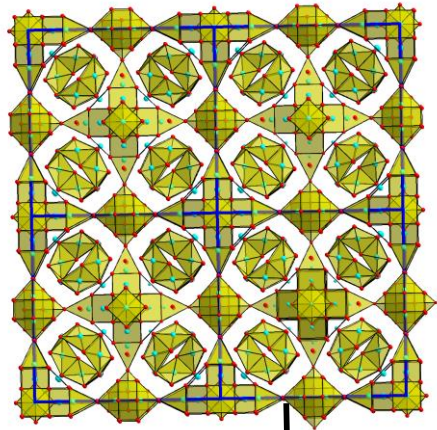
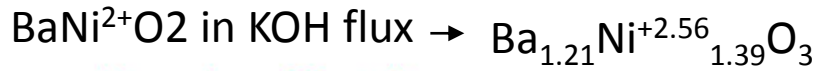
The hidden story in BaNiO₃ to BaNiO₂ transformation: adaptive structural series and NiO exsolution†

Angel M. Arévalo-López, Marielle Huvé, Pardis Simon and Olivier Mentré *

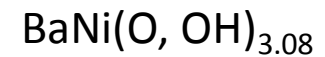
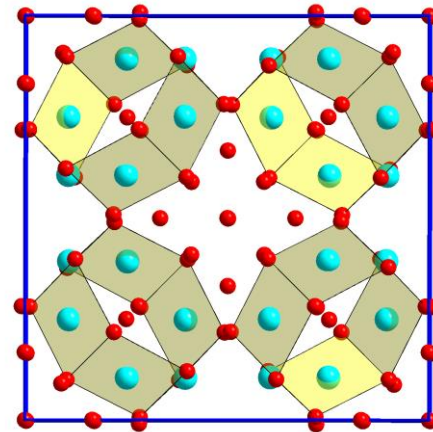
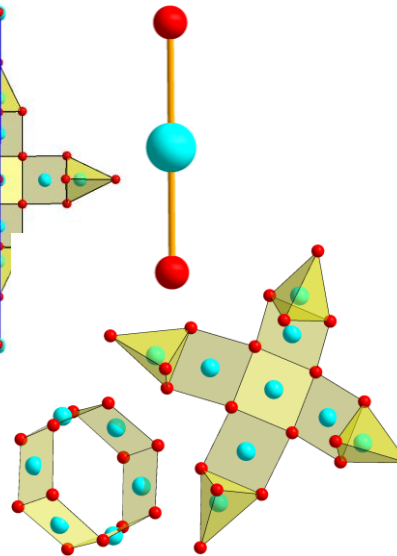
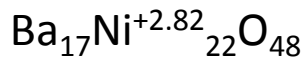
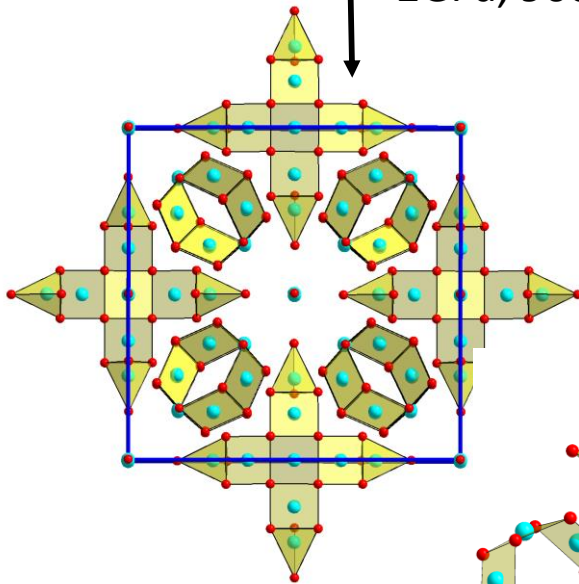


4. Some "Local" results on square-planar "exotic" Nickelates

Nickelates



2GPa, 900°C



4. Some “Local” results on square-planar “exotic” Nickelates

Journal of Solid State Chemistry 165, 214–227 (2002)

doi:10.1006/jssc.2001.9490, available online at <http://www.idealibrary.com> on IDEAL[®]

Polysynthetic Twinning Characterization and Crystallographic Refinement in $\text{NaBa}_2\text{M}_2^2+\text{M}^3+\text{O}_6$ ($M = \text{Ni}, \text{Cu}$)

Eric Quarez, Marielle Huve, Pascal Roussel, and Olivier Mentré¹

