HYDROGÈNE
accélérer l'innovation

Stratégie de recherche de nouveaux électrolytes pour pile SOFC

F. Goutenoire

SOFC Solid Oxide Fuel Cell

Anode (Oxydation)

$H_2 + O^{2-} \rightarrow H_2O + 2e-$

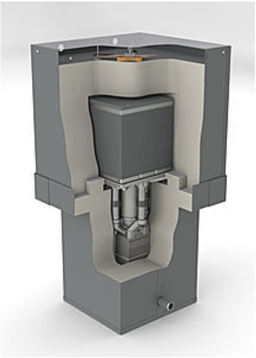
Conducteur mixte

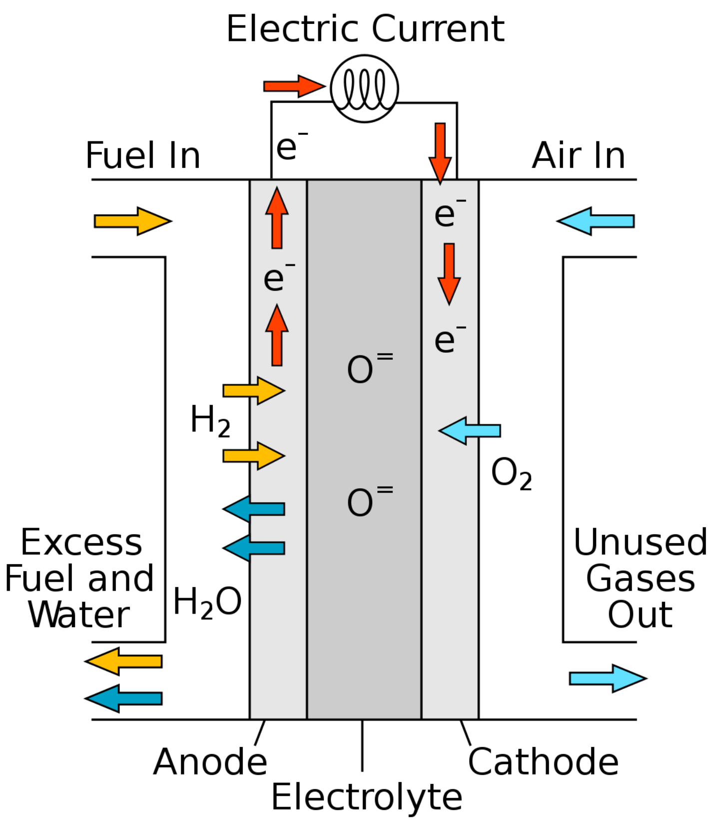
Bonne tenue

à la réduction

Cermet Ni-YSZ

$La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O_3$ (LSCM)





Bonne conduction ionique

et conduction électronique nulle

YSZ 8%Yttrium / Cérine (Gd)

Cathode (Réduction)

$\frac{1}{2} O_2 + 2e- \rightarrow O^{2-}$

Conducteur mixte

LSM

Lanthanum

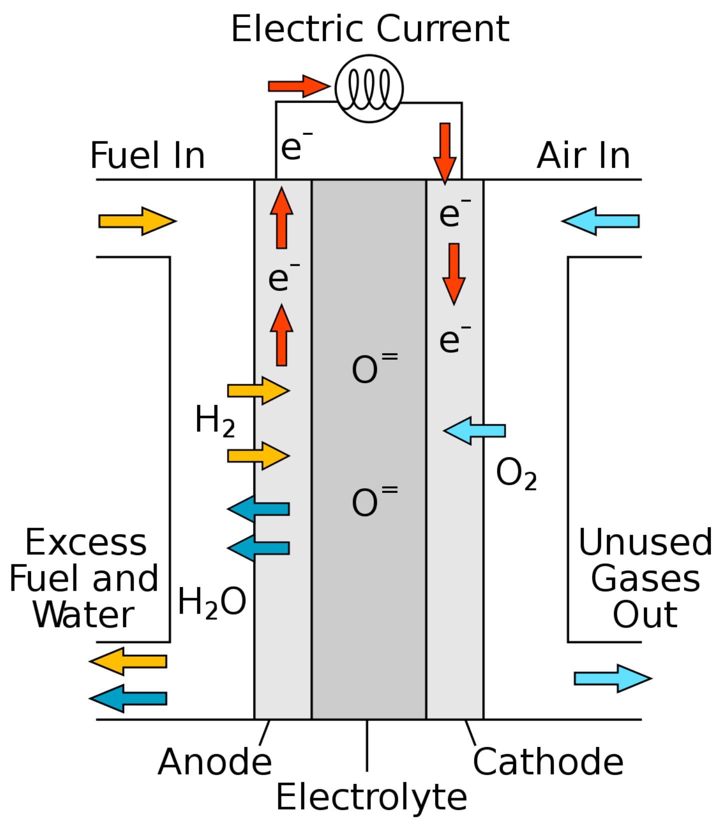
Strontium

Manganite

Source : wikipedia

SOFC Solid Oxide Fuel Cell

Verrous technologiques :
durabilité dans le temps
Temp. fonctionnement
T~1000°C
dégradation de la pile à cause des phénomènes de diffusion d'espèces

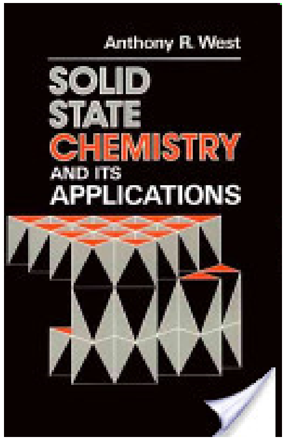


Solutions
IT-SOFC (600-700 °C)
diminuer la température de fonctionnement pour diminuer les phénomènes de diffusion
Problème: il faut trouver de meilleurs électrolytes

Source : wikipedia

Etat des lieux

Perspectives matériaux conducteurs ioniques



" Solid State Chemistry and its applications "
par Anthony R. WEST (1991)

13.2.5 Search for new electrolytes.

"Since the mid 1960s, a very active field of research has been the investigation of known and new materials for solid electrolyte behavior. Many of these searches have been carried out on a 'try it and see' basis because the crystal structures of the materials were not known. .."

"Although many theories have been proposed to account for solid electrolyte, it is still very difficult to make a priori reliable predictions ..."

Les indications :

a) un nombre important d'espèces mobiles $\sigma = ne\mu$

b) un nombre important de lacunes ⍰

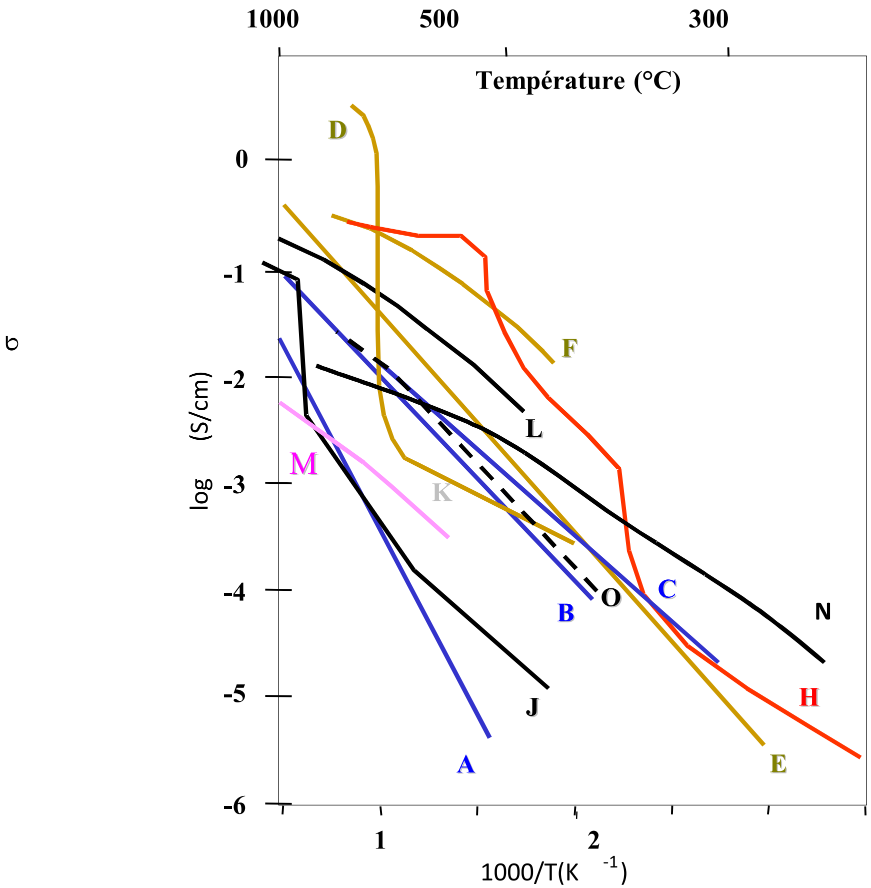
c) barrière d'énergie faible entre un site occupé et un site vide

d) une conduction tridimensionnelle

e) des atomes fortement polarisables

Etat des lieux

Comparaison des conductivités des principaux conducteurs anioniques.



<u>Zircones stabilisées :</u>

B et C: par Y_2O_3

A: par 12%CaO

<u>Bi_2O_3dopé :</u>

D: Bi_2O_3

E et F: Bi_2O_3 dopé Y_2O_3

<u>Intercroissance Bi_2O_2-Pérovskite :</u>

H: $Bi_4V_2O_{11}$

<u>Pérovskites et Brownmillérites :</u>

J:$Ba_2In_2O_5$

K:$Ba_2In_{1.75}Ce_{0.25}O_{5.125}$

L: $La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{2.9}$

<u>Pyrochlore:</u>

M: $Gd_2Ti_2O_7$

<u>Apatite:</u>

N: $La_{10}Si_6O_{27}$

<u>Scheelite:</u>

O: $Pb_{0.9}La_{0.07}WO_{4+delta}$

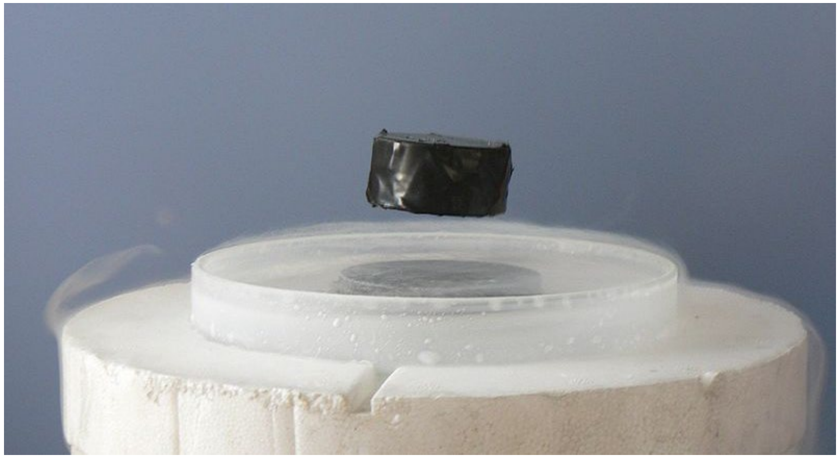
Composés avec des transitions de phase

gros cations

charge élevée

l'intérêt de recherche de nouveaux édifices structuraux

La Cristallochimie est avant tout une recherche fondamentale !

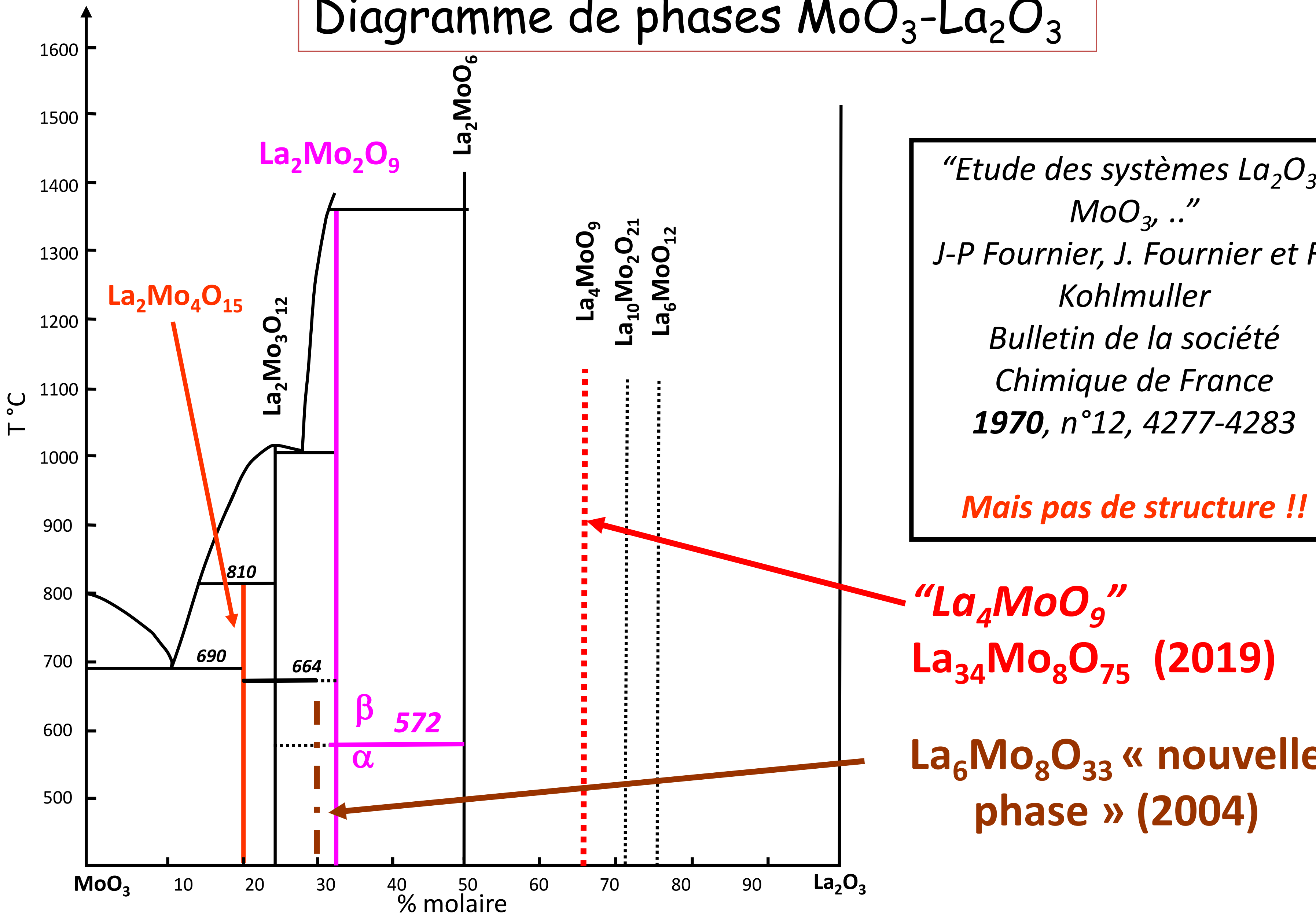


J.G. Bednorz et K.A. Müller
« Possible highT_c superconductivity in the Ba-La-Cu-O system »,
Z. Physik, B, vol. 64, nº 2, 1986, p. 189-193

Supraconductivité à 35K !!
Alors que la théorie prévoyait
une température maximale de 23K

l' intérêt de recherche de nouveaux édifices structuraux

Diagramme de phases MoO_3-La_2O_3

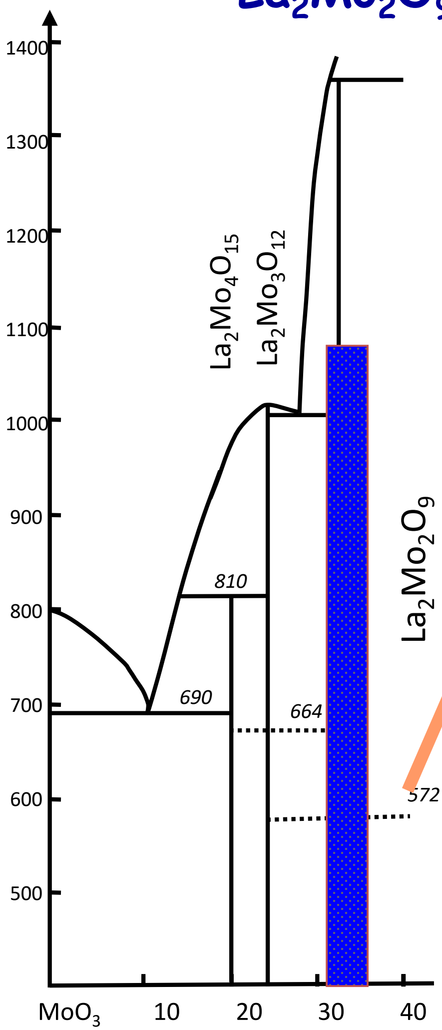


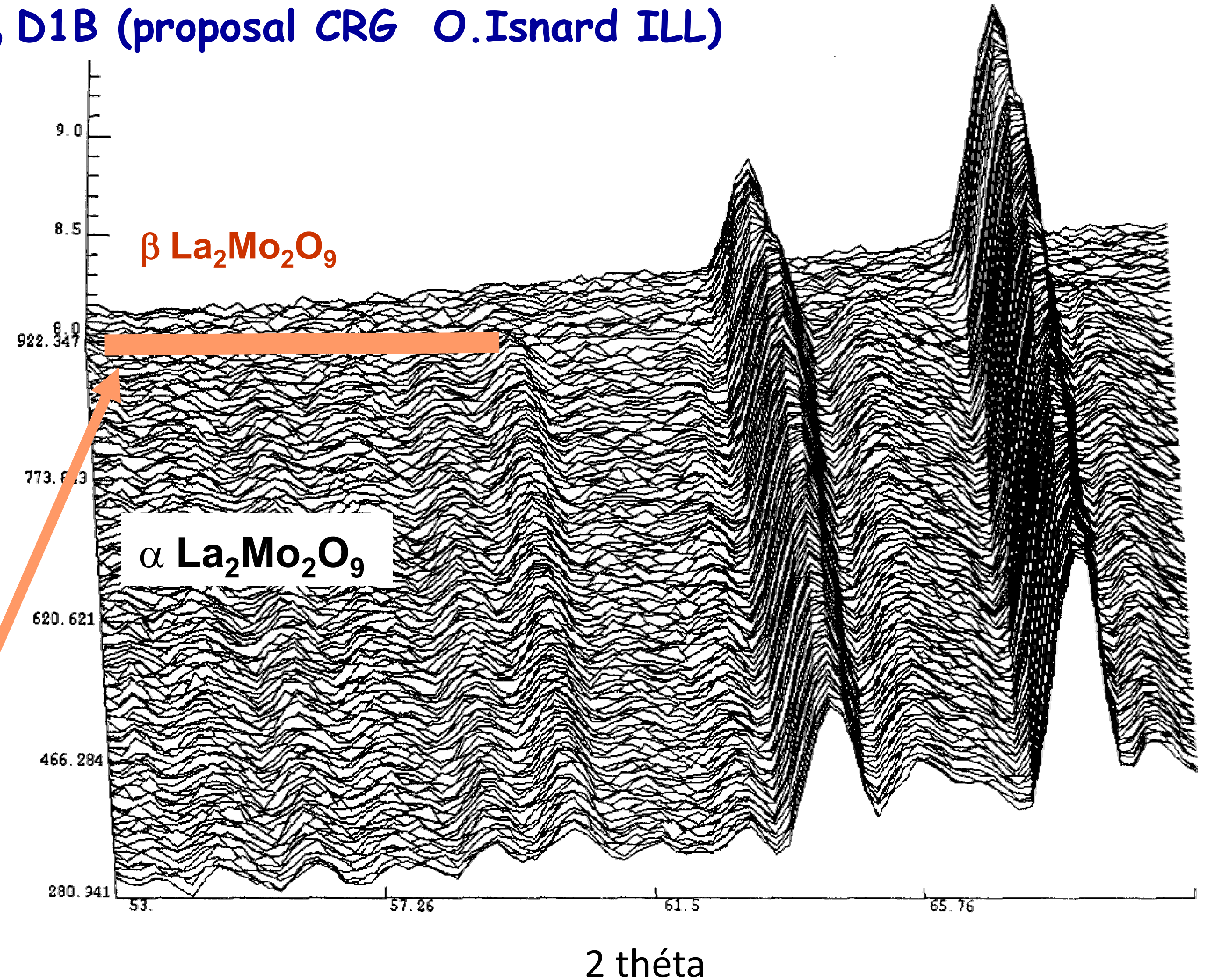
"Etude des systèmes La_2O_3-MoO_3, .."
J-P Fournier, J. Fournier et R. Kohlmuller
Bulletin de la société Chimique de France
***1970**, n°12, 4277-4283*

Mais pas de structure !!

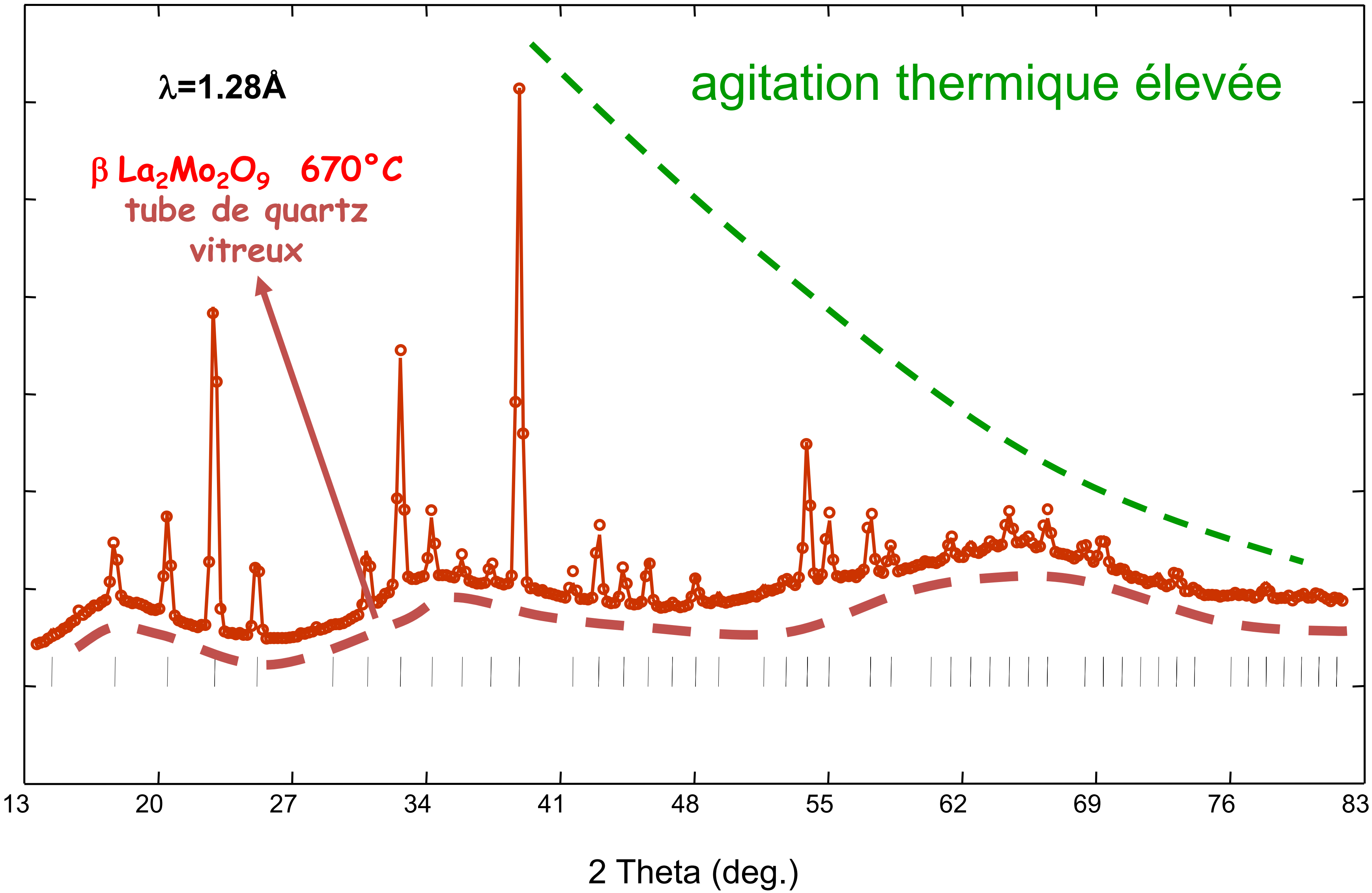
l' intérêt de recherche de nouveaux édifices structuraux

- $La_2Mo_2O_9$ D1B (proposal CRG O.Isnard ILL)

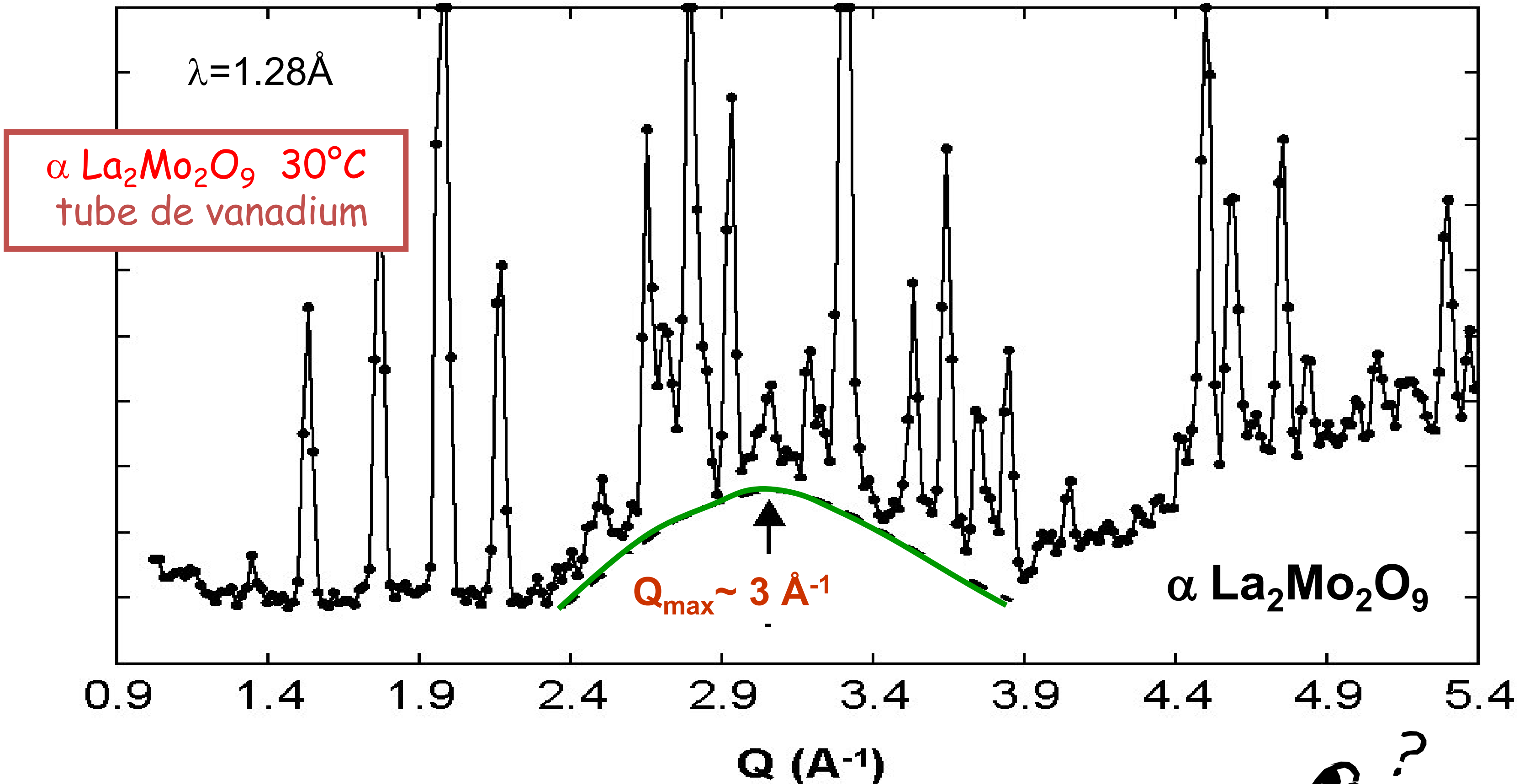




l' intérêt de recherche de nouveaux édifices structuraux



l' intérêt de recherche de nouveaux édifices structuraux



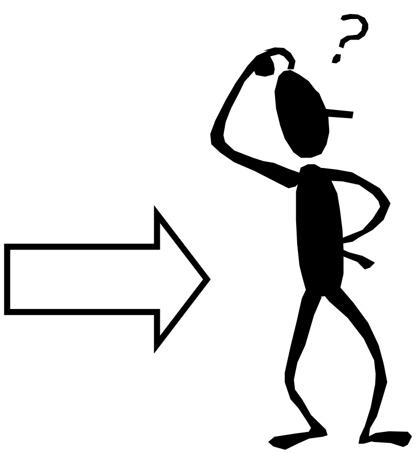
Ondulation du bruit de fond : réseau désordonné

formule de Debye :

$Q_{max} = (2\pi \times 1{,}23)/d_m$ où d_m est la distance des paires

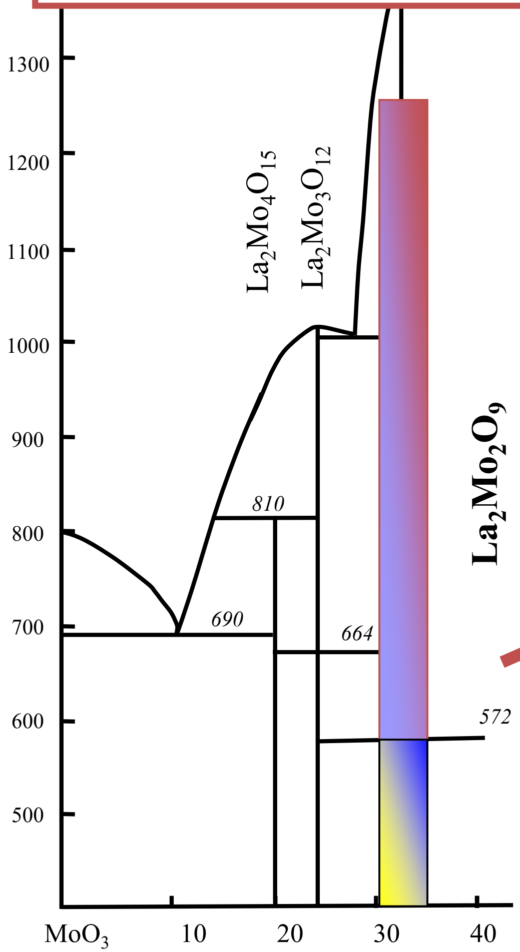
$Q_{max} \sim 3$ Å^{-1} => $d_m \sim 2{,}6$Å distance O-O minimale

=> désordre du réseau d'oxygène

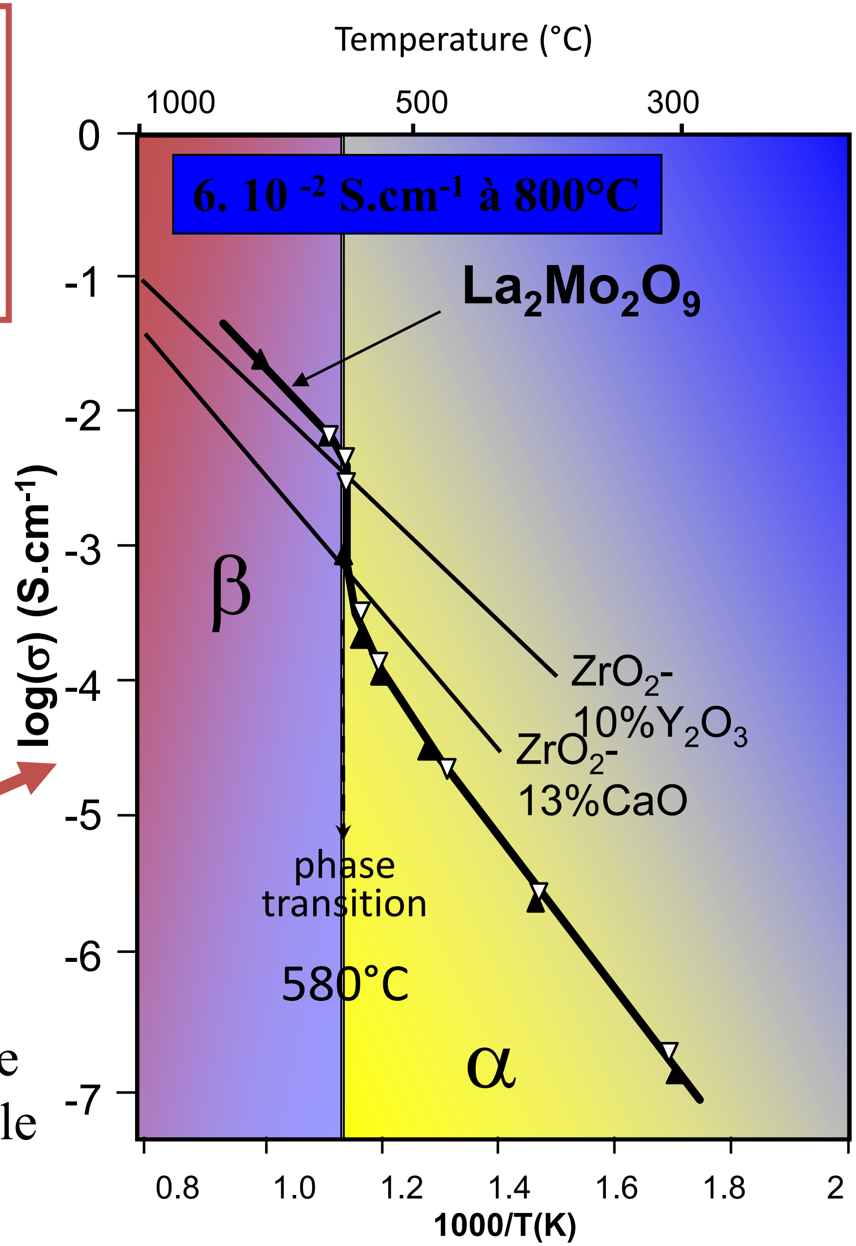


l’intérêt de recherche de nouveaux édifices structuraux

“Designing fast oxide-ion conductors based on $La_2Mo_2O_9$”
Ph. Lacorre, F. Goutenoire, O. Bohnke, R. Retoux and Y. Laligant
Nature, 2000, 404, 856-858



Détermination de structure très facile



Propriétés physiques (conduction ionique)

Ceramic technology

Oxide-ion conductors by design

John B. Goodenough

Oxide-ion conductors are solid oxides that contain highly mobile oxide ions. Some, the oxide-ion electrolytes, are electronic insulators; others are mixed oxide-ion/electronic conductors. These materials form the basis of devices that have a huge market potential. The solid-oxide fuel cell, for example, uses an oxide-ion electrolyte as a separator between air and fuel; combustion using mobile oxide ions in the electrolyte generates clean electric conduction at a low enough temperature to be technically useful. For example, the design of an oxide-ion electrolyte that would allow operation of a solid oxide fuel cell at 600–700 °C has motivated chemists for a number of years; the goal has not yet been reached, and new design concepts are needed. On page 856 of this issue, Lacorre *et al.*[1] report a novel oxide-ion electrolyte that introduces a large structural family to be explored.

Nature, 404, 20 Avril 2000, page 821

The Nobel Prize in Chemistry 2019

Prize motivation: "for the development of lithium-ion batteries."

Bilan Brevets/Thèses

2 brevets / 5 thèses

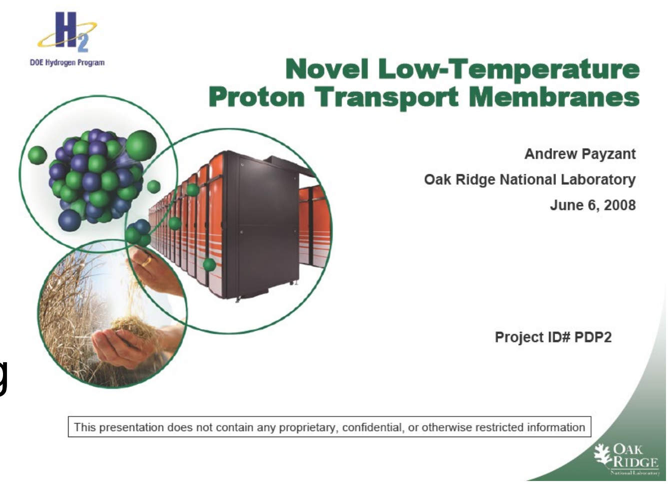
Conduction O^{2-} (Lacorre, Goutenoire) (2000)

Co-catalyse (Lacorre, Millet IRC Lyon) (2007)

600 citations

Financement ?

Conduction H^+ (Andrew Payzant) (2005)



Budget 2004-2008

700 K$

US 7,413,687 B2 Low temperature proton conducting oxide devices , A. Payzant, Oak Ridge, Tenn. (US)

Okapi ConducThor (2017)

Ph. Lacorre 2019…

Matériaux électrostrictifs

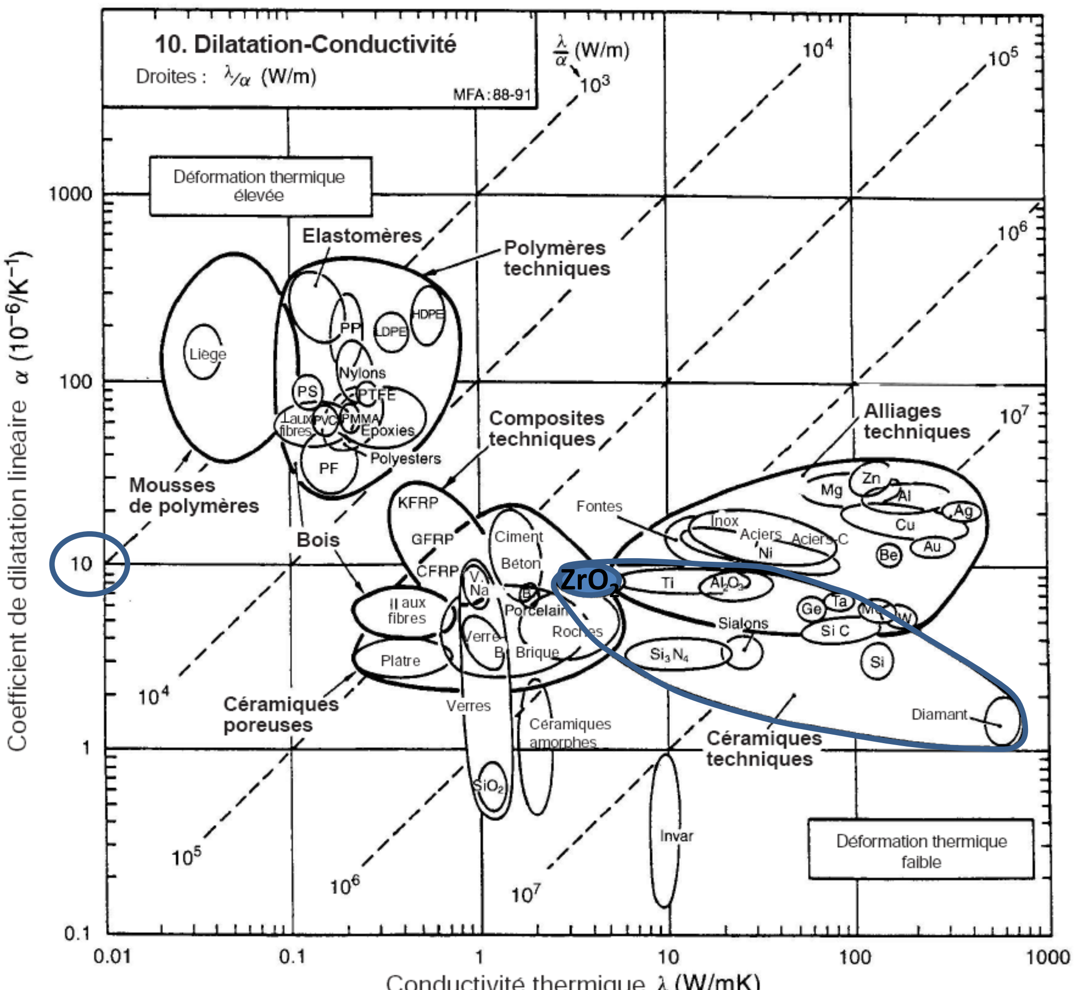
Propriétés physiques (isolant thermique haute température)

Michael F. Ashby
Choix de matériaux en construction mécanique

Oxide Materials with Low Thermal Conductivity

Michael R. Winter and David R. Clarke†

Materials Department, College of Engineering, University of California, Santa Barbara, California 93160-5050



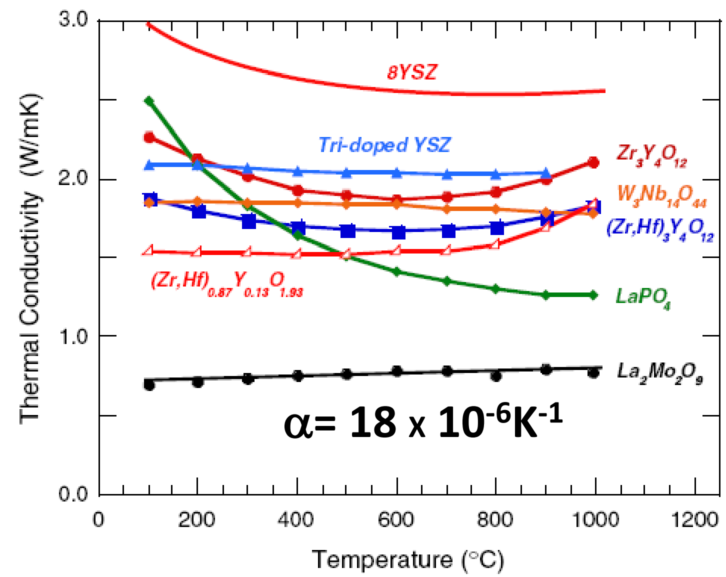


Fig. 7. Thermal conductivity of $La_2Mo_2O_9$ compared with the other materials investigated in this work. The density of the $La_2Mo_2O_9$ samples was 90%.

Propriétés physiques (électrostriction)

PHYSICAL REVIEW MATERIALS **2**, 041403(R) (2018)

Rapid Communications

Giant thermally-enhanced electrostriction and polar surface phase in $La_2Mo_2O_9$ oxygen ion conductors

Qian Li,[1,2,*] Teng Lu,[3] Jason Schiemer,[4] Nouamane Laanait,[1] Nina Balke,[1] Zhan Zhang,[2] Yang Ren,[2] Michael A. Carpenter,[4] Haidan Wen,[2] Jiangyu Li,[5] Sergei V. Kalinin,[1] and Yun Liu[3,†]

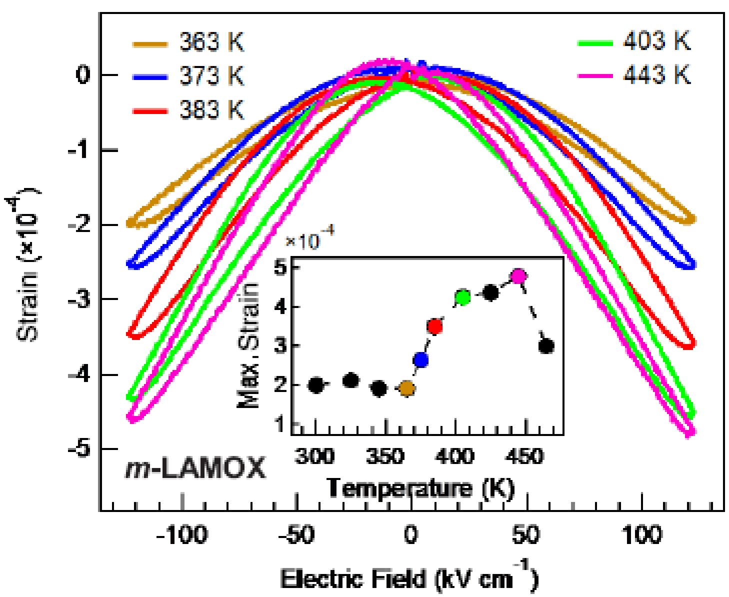
[1]*Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

[2]*X-ray Science Division, Argonne National Laboratory, Lemont, Illinois 60439, USA*

[3]*Research School of Chemistry, The Australian National University, Canberra, ACT 0200, Australia*

[4]*Department of Earth Sciences, University of Cambridge, Cambridgeshire CB2 3EQ, United Kingdom*

[5]*Department of Mechanical Engineering, University of Washington, Seattle, Washington 98195, USA*



https://en.wikipedia.org/wiki/Electrostriction#Applications

Materials [edit]

Although all dielectrics exhibit some electrostriction, certain engineered ceramics, known as relaxor ferroelectrics, have extraordinarily high constants. The most commonly used are

- lead magnesium niobate (PMN)
- lead magnesium niobate-lead titanate (PMN-PT)
- lead lanthanum zirconate titanate (PLZT)

Magnitude of effect [edit]

Electrostriction can produce a strain of 0.1% at a field strength of 2 million volts per meter (2 MV/m) for the material called PMN-15 (TRS webs references below). The effect appears to be quadratic at low field strengths (up to 0.3 MV/m) and roughly linear after that, up to a maximum fie MV/m[citation needed]. Therefore, devices made of such materials are normally operated around a bias voltage in order to behave nearly linearly. cause deformations to lead to a change of electric charge, but this is unconfirm

Applications [edit]

- Sonar projectors for submarines and surface vessels
- Actuators for small displacements

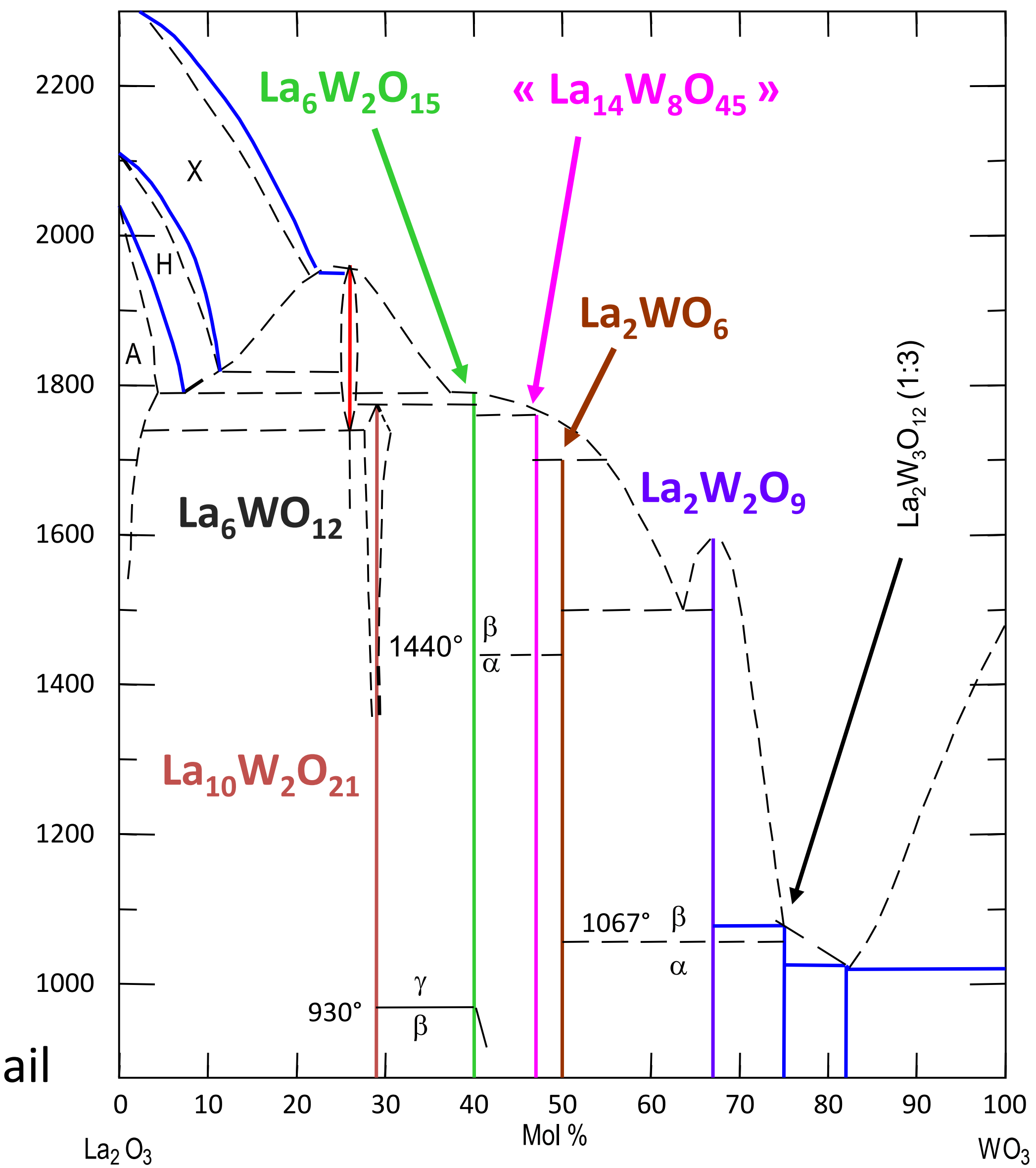
l' intérêt de recherche de nouveaux édifices structuraux

Diagramme de phases // La_2O_3-WO_3
étude structurale

-System La_2O_3-WO_3. High-temperature phase diagram, especially in the region 75-100 mol% La_2O_3. A, H, and X = rare-earth structure types.
M. Yoshimura and A. Rouanet, *Mater. Res. Bull.*, **11** [2] 151-158 (1976).

Analyse structurale au sein du diagramme de phase La_2O_3-WO_3 et exploration des propriétés de conduction ionique.
Thèse Marie-Hélène Chambrier
2006-2009 (SUDOC)

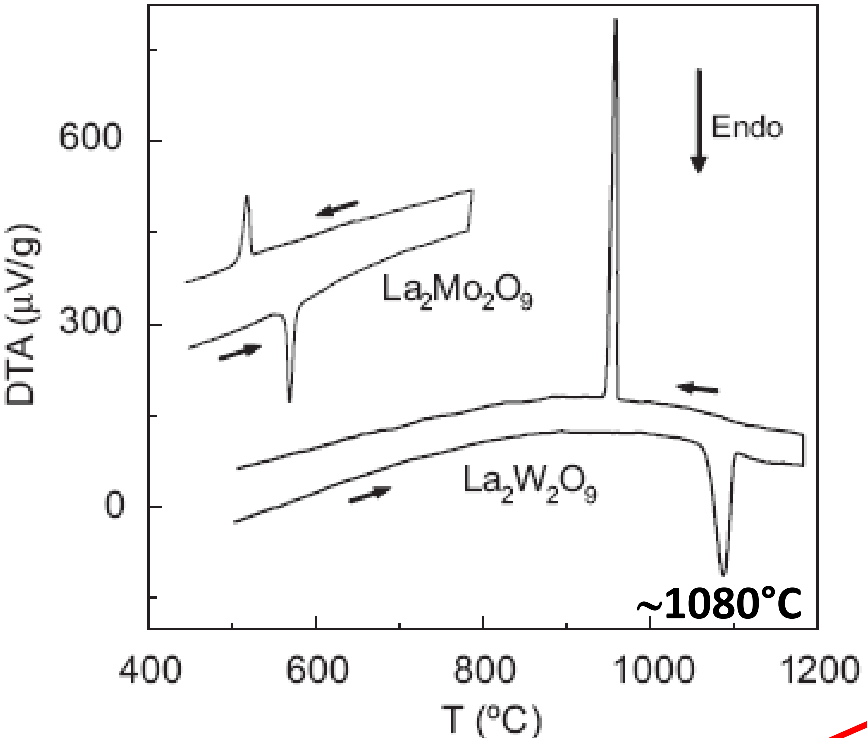
Résolutions structurales :
$La_6W_2O_{15}$ (gamma)
$La_{18}W_{10}O_{57}$; La_2WO_6 (alpha-beta) ; nouvelle phase à 41 % et $La_{10}W_2O_{21}$
$La_2W_2O_9$ (alpha) Y. Laligant et A. LeBail

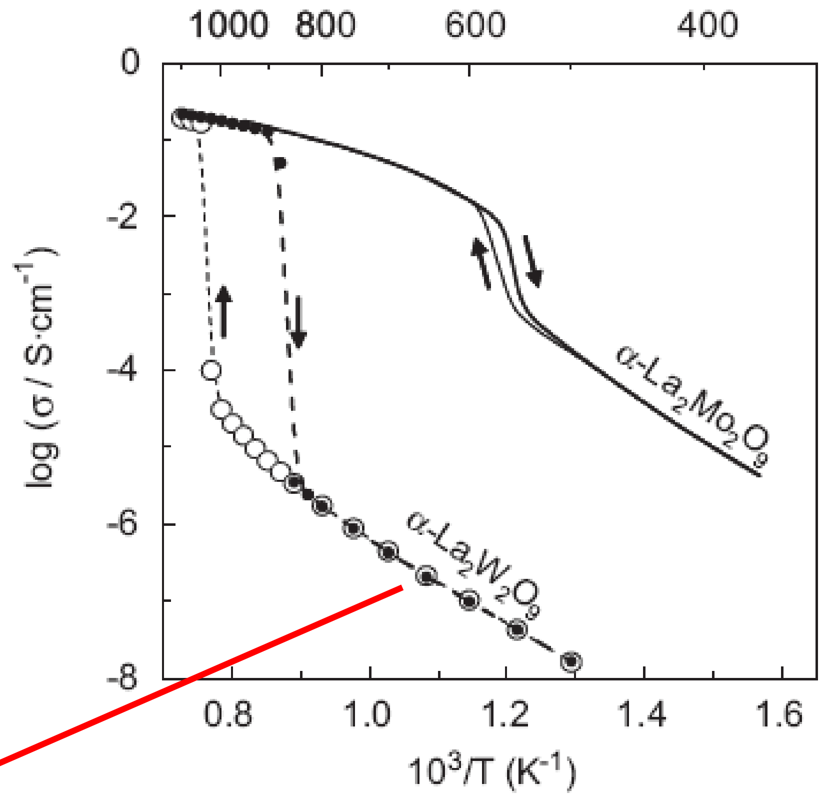


Propriété physique (conduction ionique)

$La_2W_2O_9$

Phase stability and ionic conductivity in substituted $La_2W_2O_9$,
D. Marrero-Lopez, J. Pena-Martınez, J.C. Ruiz-Morales, P. Nunez
Journal of Solid State Chemistry 181 (2008) 253–262.





« Ab-initio structure determination of $La_2W_2O_9$ from X-ray and neutron powder diffraction »
Yvon Laligant, Armel Le Bail et F. Goutenoire, . JSSC 159, 223-227, 2001

Propriété physique (conduction ionique)

CHEMISTRY OF MATERIALS

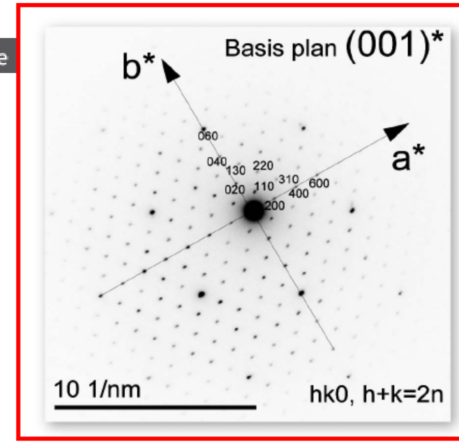
"La_4MoO_9"

$La_{34}Mo_8O_{75}$ (2019)

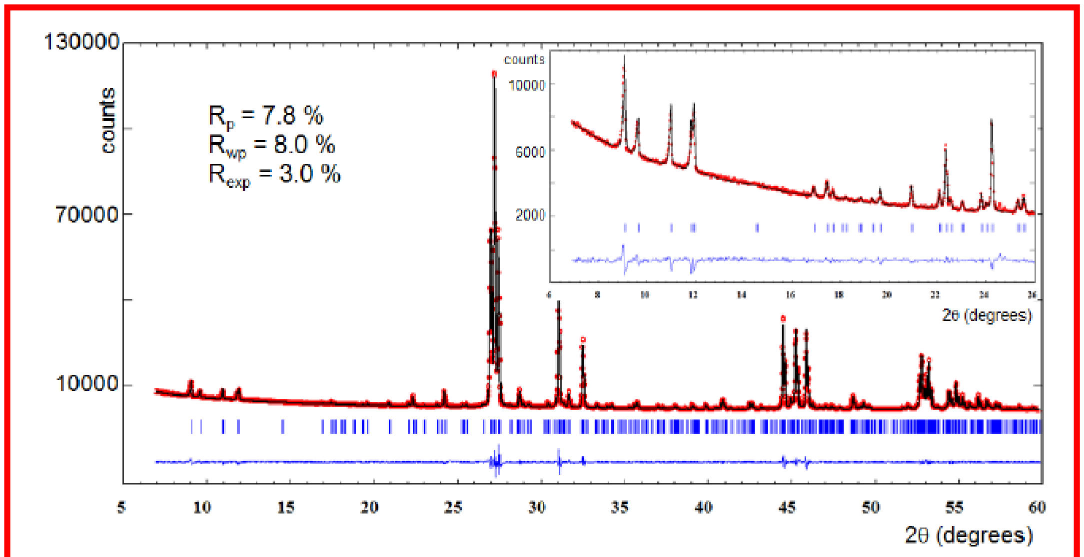
pubs.acs.org/cm Article

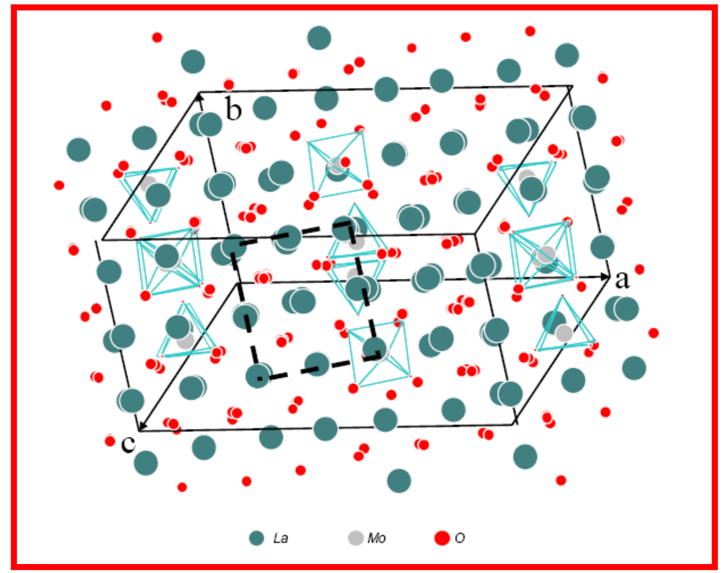
Unravelling Crystal Superstructures and Transformations in the $La_{6-x}MoO_{12-\delta}$ ($0.6 \leq x \leq 3.0$) Series: A System with Tailored Ionic/Electronic Conductivity

Adrián López-Vergara, Lucía Vizcaíno-Anaya, José M. Porras-Vázquez,* Gianguido Baldinozzi, Lucía dos Santos-Gómez, Jesús Canales-Vazquez, David Marrero-López, and Enrique R. Losilla



Conduction mixte (H^+/e-) 5 $mS.cm^{-1}$ pour $La_{5.4}MoO_{11.1}$ et 9.5 $mS.cm^{-1}$ pour La_4MoO_9 à 700°C

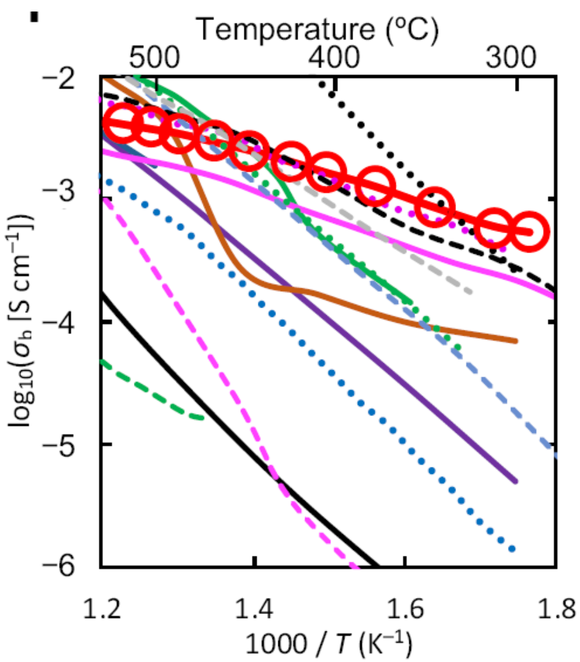




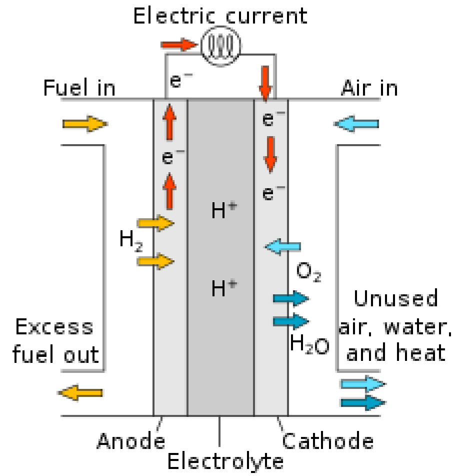
Propriété physique (conduction ionique)

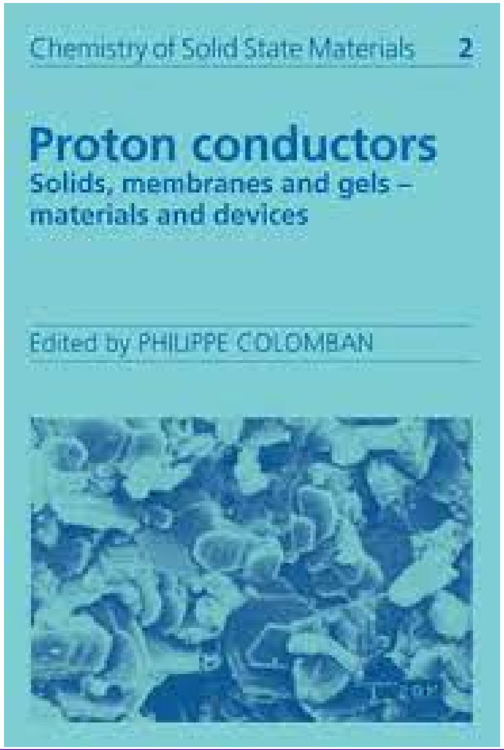
PEMFC Polymer exchange membrane Fuel Cell

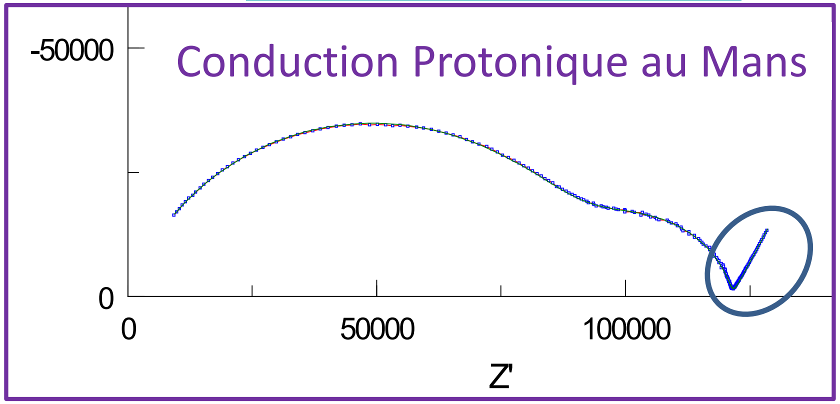
Limitation
Température ~ 85°C
H_2O est liquide
$(H_2O)_nH^+$

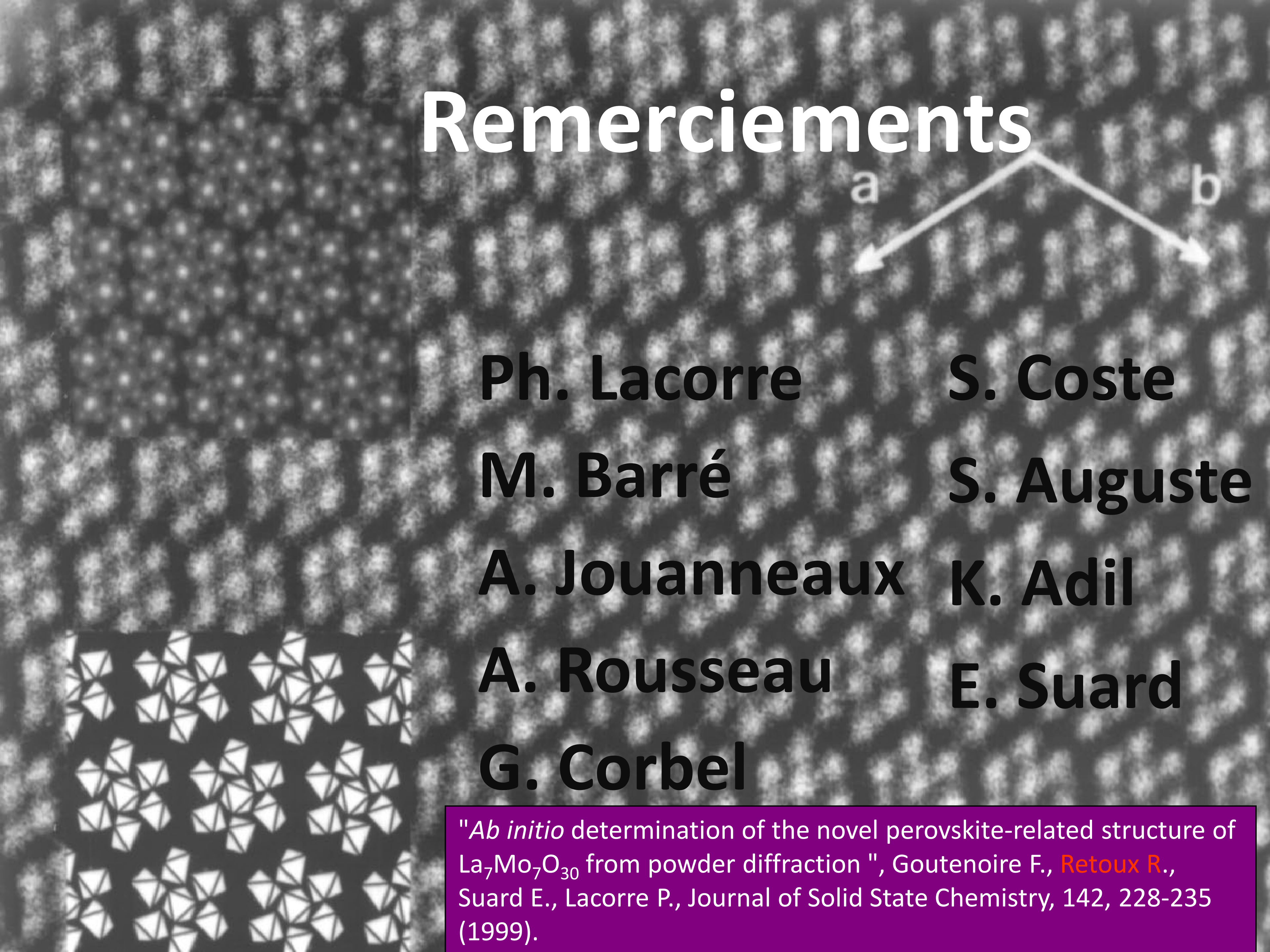


$Ba_7Nb_{3.9}Mo_{1.1}O_{20.0}$ (Nat. Comm Skinner 2020)









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K. Adil
E. Suard

"*Ab initio* determination of the novel perovskite-related structure of $La_7Mo_7O_{30}$ from powder diffraction ", Goutenoire F., Retoux R., Suard E., Lacorre P., Journal of Solid State Chemistry, 142, 228-235 (1999).

Propriétés physiques (conduction ionique)

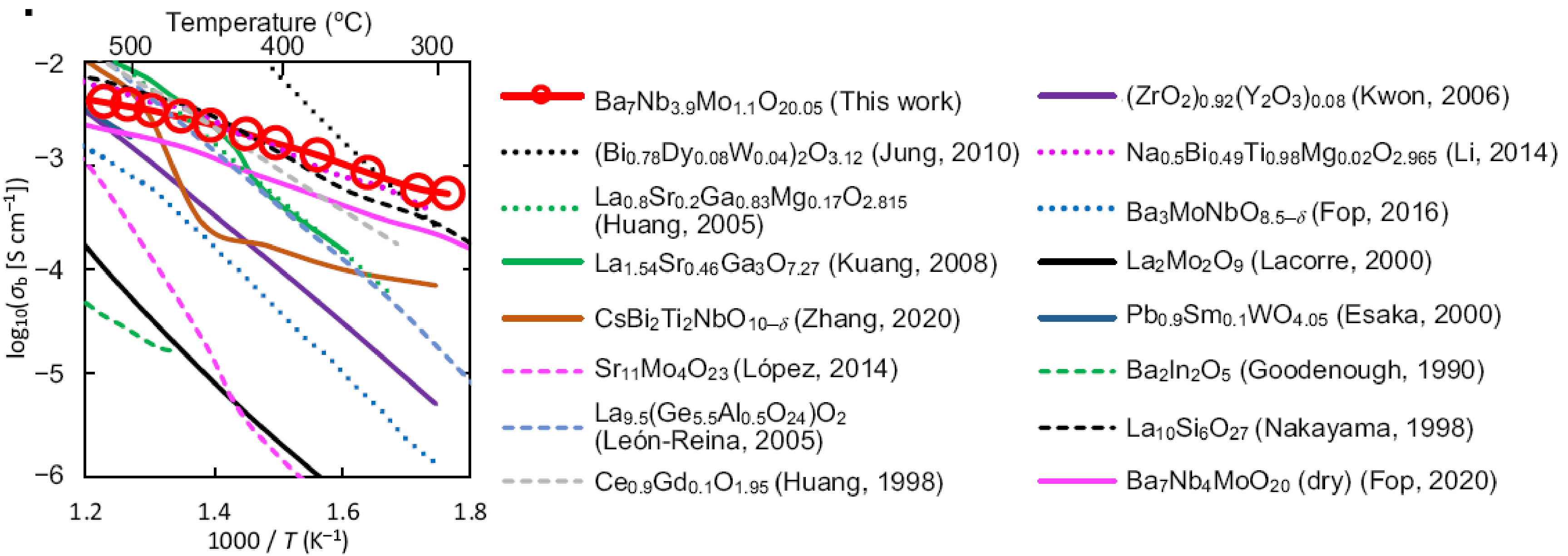

Fig. 1 High oxide-ion conductivity of $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$. a, **b** Complex impedance plots of $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$ recorded in dry air at (**a**) 309 °C and (**b**) 598 °C. **c** Arrhenius plots of bulk conductivity σ_b, grain-boundary conductivity σ_{gb} and DC σ_{tot} of $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$ in dry air. Activation energy for σ_b of $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$ decreases with temperature from 0.454 to 0.185 eV as shown by the red numbers in panel c. Green line represents σ_b of $Ba_7Nb_4MoO_{20}$ reported by Fop et al.[40]. **d** Oxygen transport number of $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$. **e** Oxygen partial pressure $P(O_2)$ dependence of σ_{tot} of $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$. **f** Comparison of bulk conductivities of $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$ and other oxide-ion conductors.