Proton in Perovskites: content, structural distortions and dynamics - neutron scattering study

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Laboratoire de Dynamique, Interactions et Réactivité

Context

perovskite ceramic

$M(Ba,Sr)B(Zr,Ce,Ti)_{1-x}O_{3-\delta}Ln/RE_yH_z$

⇩

Proton conductor in middle temperature range

⇩

Huge industrial potential:

Hydrogen Economy

⇩

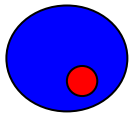
Complex physical-chemical behaviour ➔ many discrepancies in literature

- content of bulk protonic species
- bulk proton nature
- structural modifications
- bulk proton dynamics

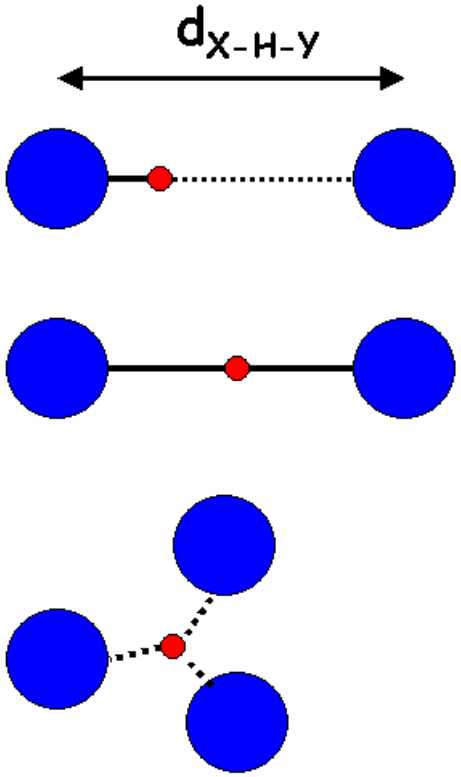
« The physics and chemistry of proton are unique »

Ph. Colomban, Proton Conductors, Cambridge University Press, 1992

Proton size: electron < H^+ < Li^+ ion



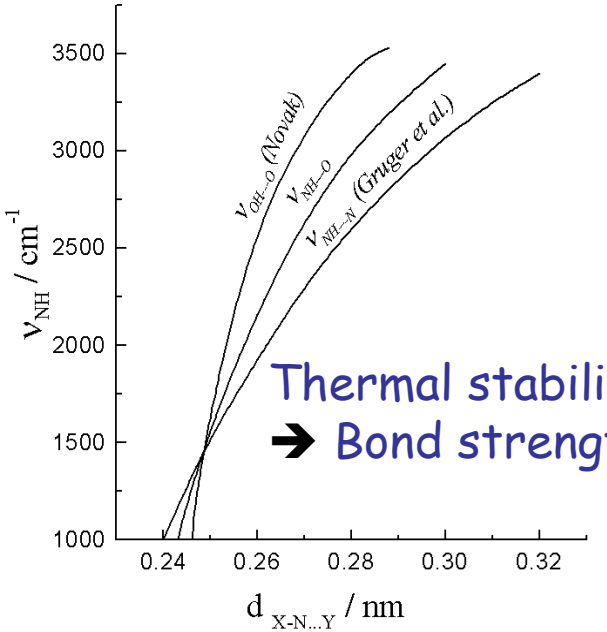
acceptor covalence shell penetration
(OH^-, H_3O^+, NH_4^+)



weak asymmetric H-bond

strong symmetric H-bond

ionic proton



Thermal stability
➔ Bond strength

Extremely complex behaviour of Protonics

High complexity of Protonics ➔ specific methods of analysis

H: σ_{incoh} = 80.26 barns; σ_{coh} = 1.76 barns

- direct measurement of proton content
- local and long range proton motion, proton dynamics: QENS (meV-μeV)
- host structure modifications, proton location: Diffraction
- proton nature, possibility of ionic proton detection! INS

Neutron measurements should be performed on:

- good quality samples = high dense ceramics, mechanically and chemically stable in operating conditions
- in operating conditions

Samples and Experiments

high dense (97-99%) ceramics stable in operating conditions

$(Ba,Sr)Zr_{1-x}Ln_xO_{3-\delta}H_z$

$BaZr_{0.94}Ln_{0.06}O_{3-\delta}H_{0.005}$ (97%) BZ_6

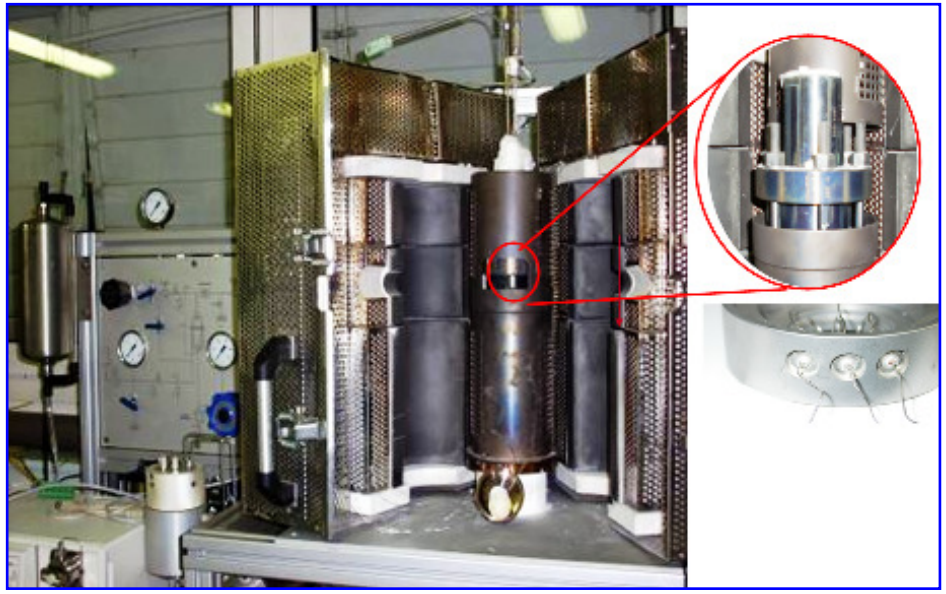
$SrZr_{0.93}Ln_{0.07}O_{3-\delta}H_{0.003}$ (98%) SZ

$BaZr_{0.97}Ln_{0.03}O_{3-\delta}H_{0.001}$ (99%) BZ_3

$SrZr_{0.93}Ln_{0.07}O_{3-\delta}H_{0.004}$ (99%) SZ

protonated in autoclaves at high temperature, under high H_2O vapour pressure

➔ **water steam electrolysis conditions**



Stable electrolytes allowing hydrogen production

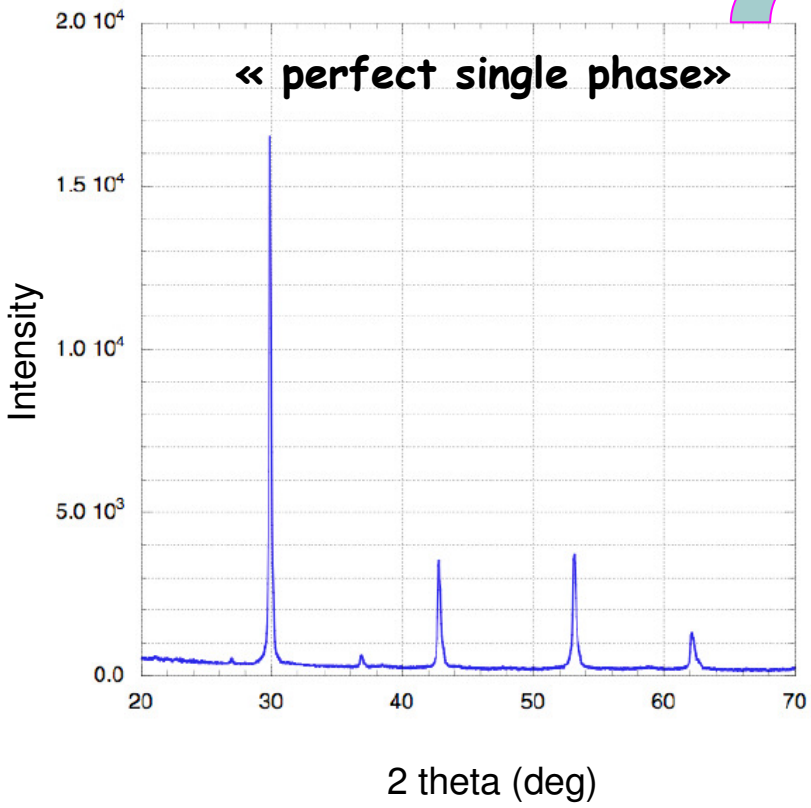
(PCT patent WO 2008/152317 A2 (18-12-2008)

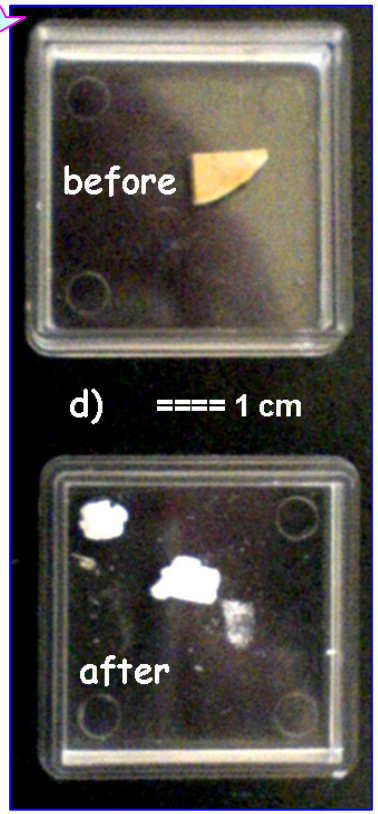
AREVA NP, Montpellier FRANCE

Importance of sample processing

$BaZr_{0.25}In_{0.75}O_{3-\delta}$ (cooperation Northern Univ. - Argonne Laboratory)

chemical and mechanical decomposition; premature aging





$BaZr_{0.25}In_{0.75}O_{3-\delta}$

300°C
80 bar
5 days

$Ba(OH)_2$, H_2O +

+ $BaCO_3$ + ZrO_2

Idem other Ln-modified perovskites !

A. Slodczyk et al. MRS Proceedings 1311 (2011)

Samples and Experiments

high dense (97-99%) ceramics stable in operating conditions

$(Ba,Sr)Zr_{1-x}Ln_xO_{3-\delta}H_z$

(PCT patent WO 2008/152317 A2 (18-12-2008)

neutron diffraction : G 41 Cold Neutron Two Axis Diffractometer PYRRHIAS
25 – 900°C

quasi-elastic neutron scattering **300 – 1200°C**

1T1 Double Focusing Thermal 3 Axis Spectrometer
4F1 Cold Neutron 3 Axis Spectrometer
} 3-axis

Time-of-flight Mibemol Spectrometer TOF

inelastic neutron scattering: Time-of-flight Mibemol Spectrometer

neutronography

LLB CNRS-CEA
Saclay, France

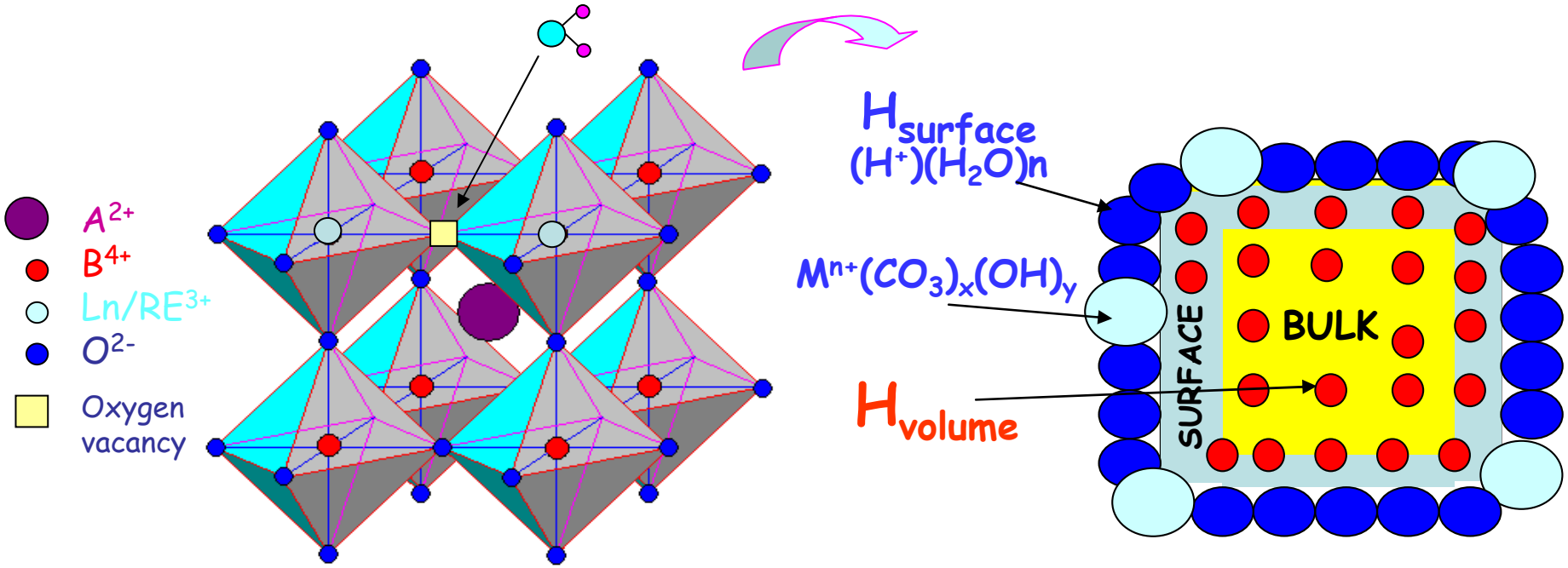
thermogravimetric analysis (He atmosphere; Pt crucible)

IR transmission (polished ceramics ~ 150μm)

***in situ* Raman scattering**: autoclave with sapphire window (20-600°C, 20 bars H_2O)

***in situ* Conductivity** : water steam electrolyser (20-600°C, 20 bars H_2O)

Complexity of protonation process



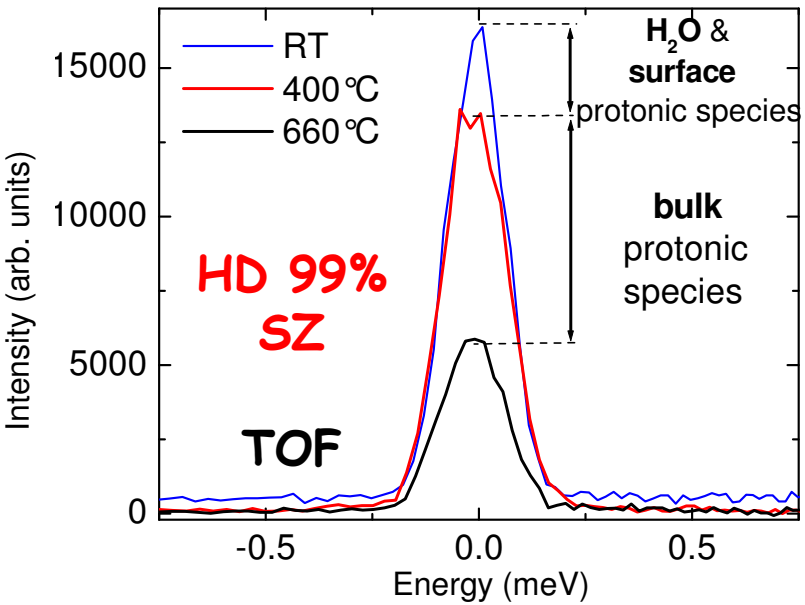
Successful protonation depends on:

- a sample composition (oxygen vacancy content, A - element)
- a sample density/active surface area
- protonation conditions (time, pressure, temperature)

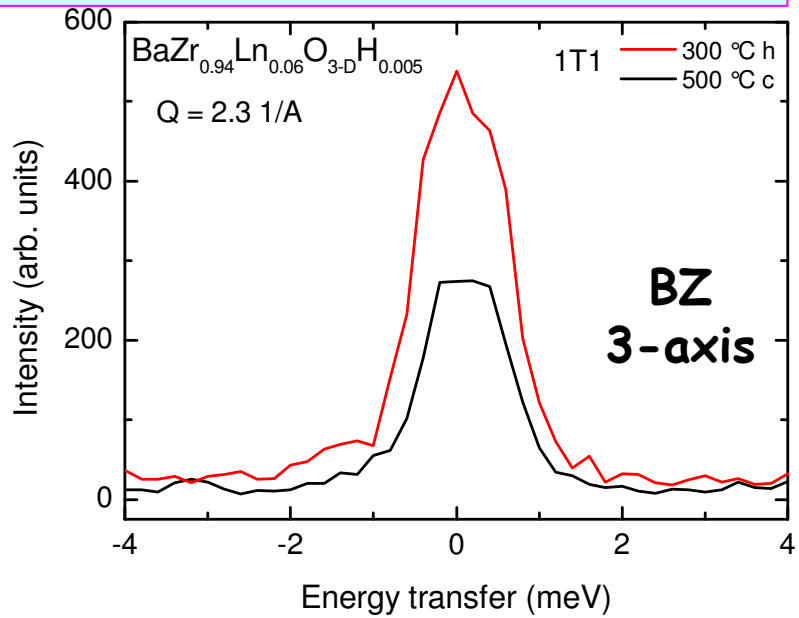
Quantitative and qualitative control of the protonation ➔ differentiation between the surface and bulk protons is necessary!

Ph. Colomban, A. Slodczyk Membranes 2, 493 (2012)

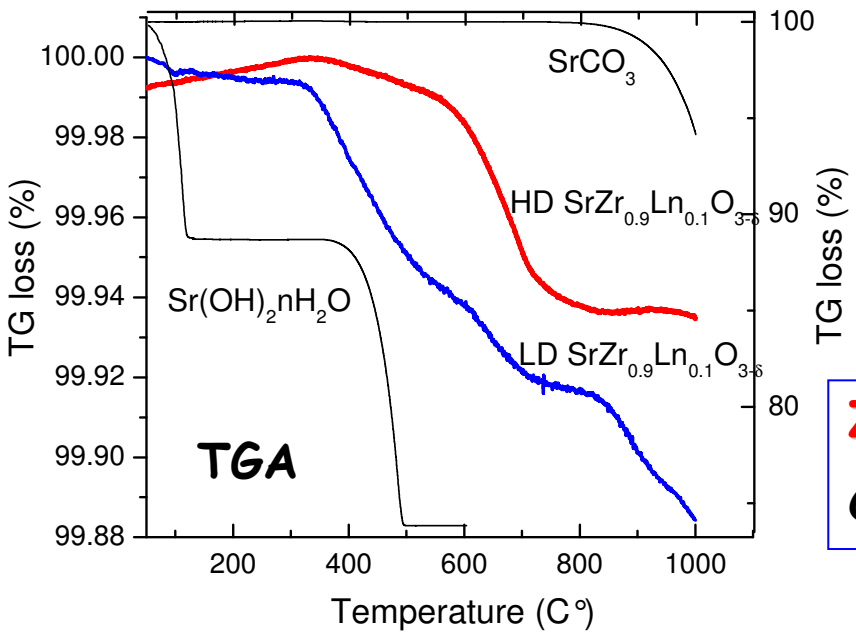
Content of protonic species – differentiation between bulk and surface



A. Slodczyk et al. MRS Proceedings 1309 (2011)



A. Slodczyk et al. J. Mater. Research 27, 1939 (2012)



$BaZr_{0.94}Ln_{0.06}O_{3-\delta}H_{0.005}$ (97%)

$SrZr_{0.93}Ln_{0.07}O_{3-\delta}H_{0.004}$ (99%)

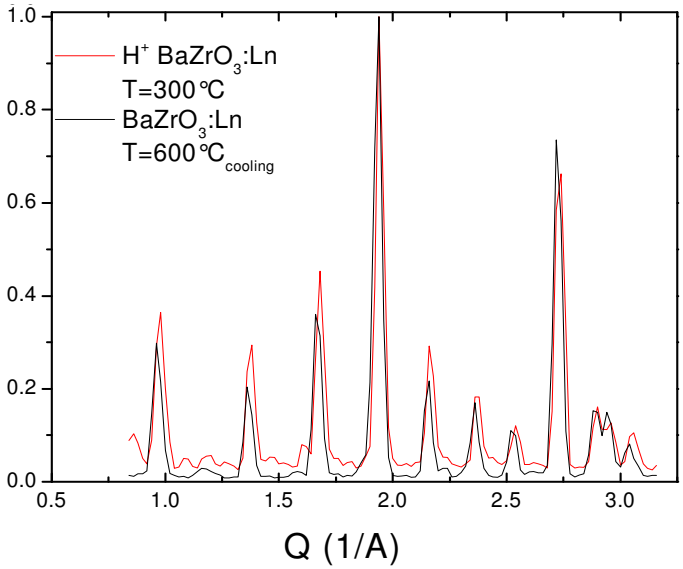
Zirconates H ~ 0.1 – 0.5 *10^{-2} mole/mole

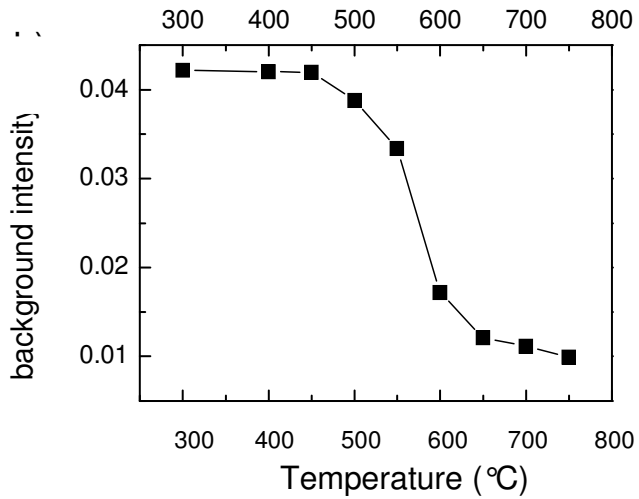
Cerates H ~ 2 *10^{-2} mole/mole

Hempelmann Phys. B 226 (1996) 72

Protonic species content

diffraction background analysis



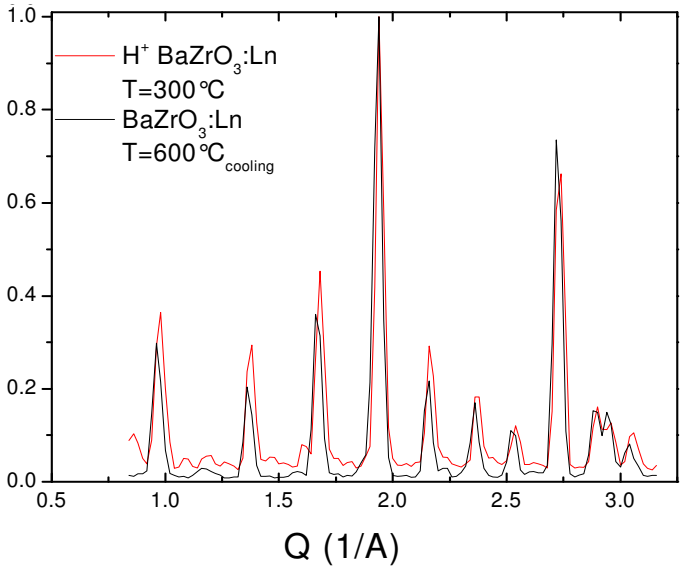


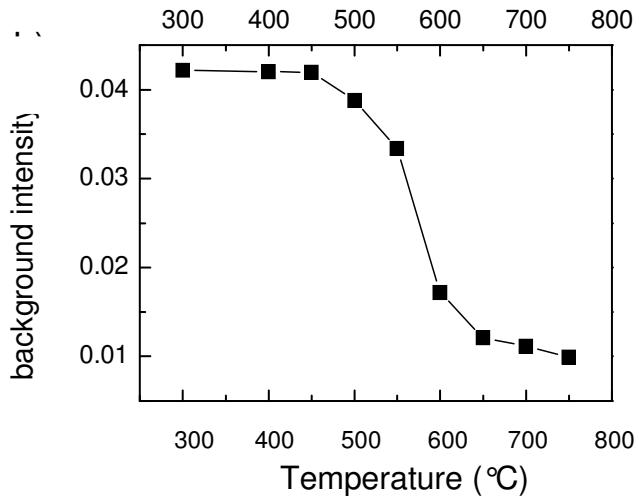
A. Slodczyk et al. J. Mater. Research 27, 1939 (2012)

A. Slodczyk et al. Solid State Ionics (2012) in press

Protonic species content

diffraction background analysis





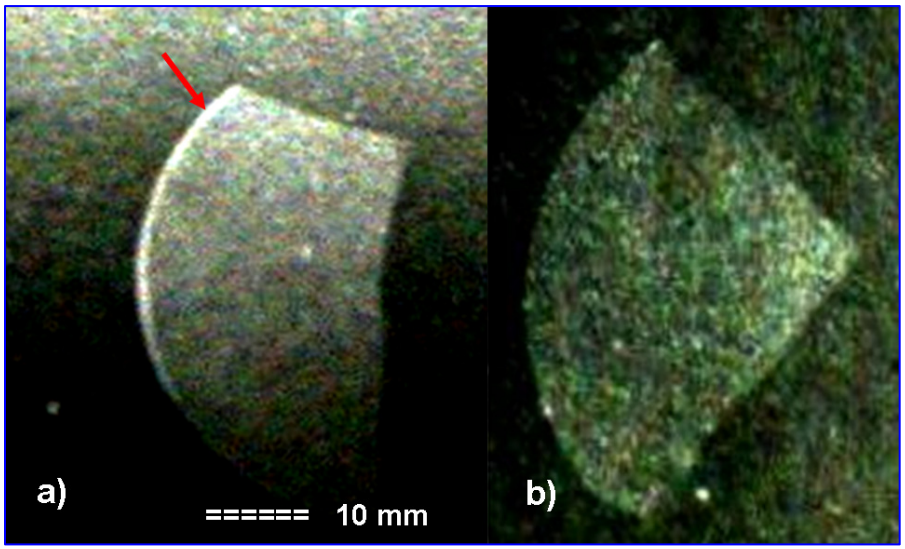
A. Slodczyk et al. J. Mater. Research 27, 1939 (2012)

A. Slodczyk et al. Solid State Ionics (2012) in press

neutronography

SZ (250°C/40bar/72h)

surface protonic species



SZ (310°C/90bar/96h)

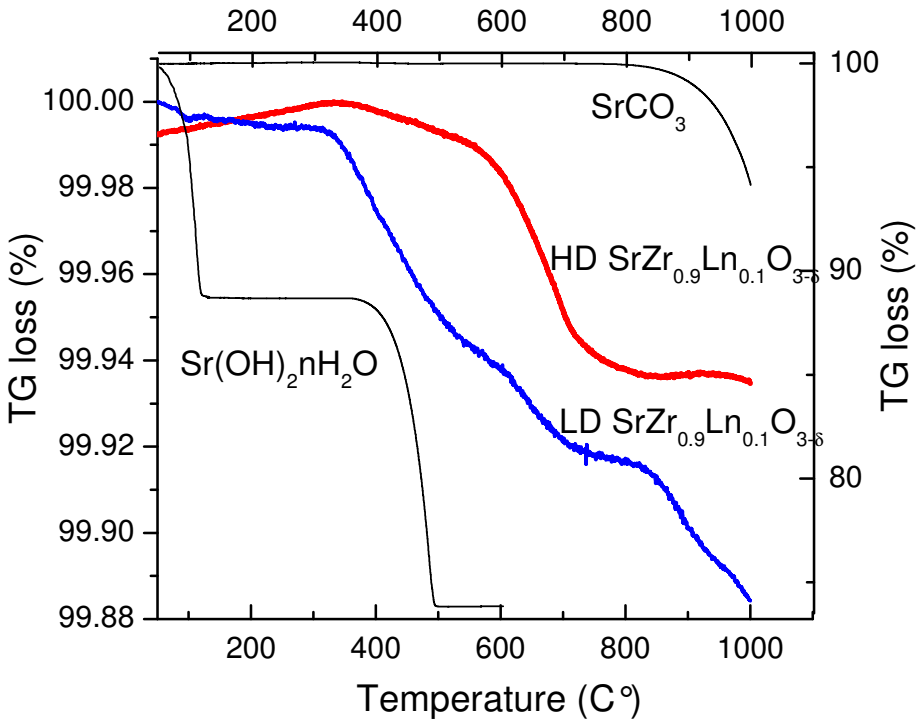
homogeneous distribution of protonic species

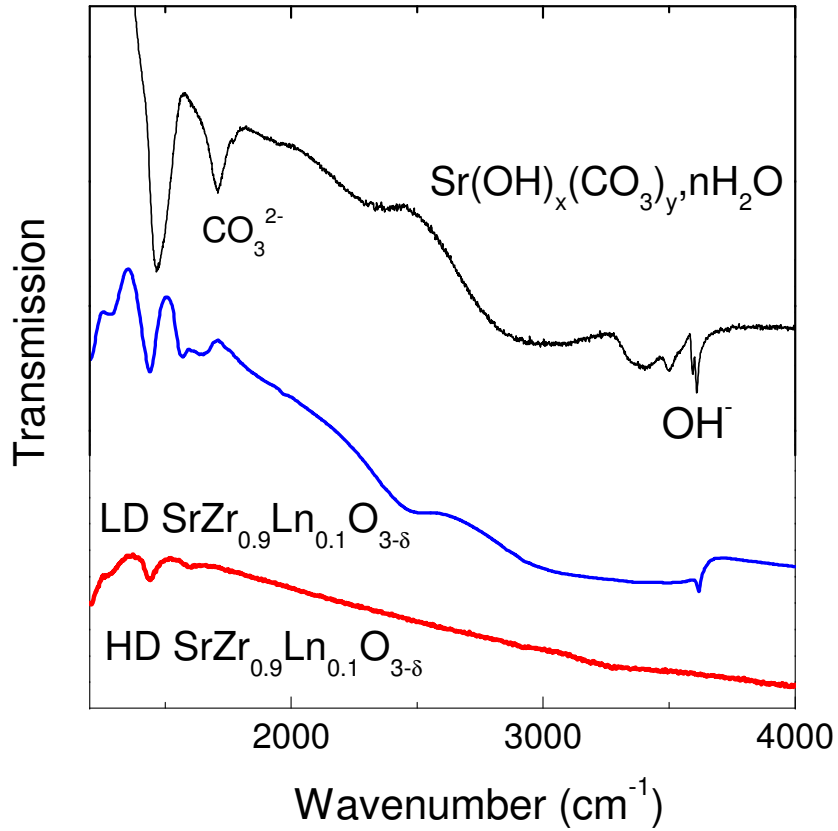
Ph. Colomban, A. Slodczyk Membranes 2, 493 (2012)

What is a nature of bulk proton? – TGA and IR approach

SZ_99% ➔ 500°C/80 bar/5 days ➔ **bulk protons**

SZ_90% ➔ 200°C/15 bar/ 5 days ➔ **surface protonic species + traces of bulk protons**

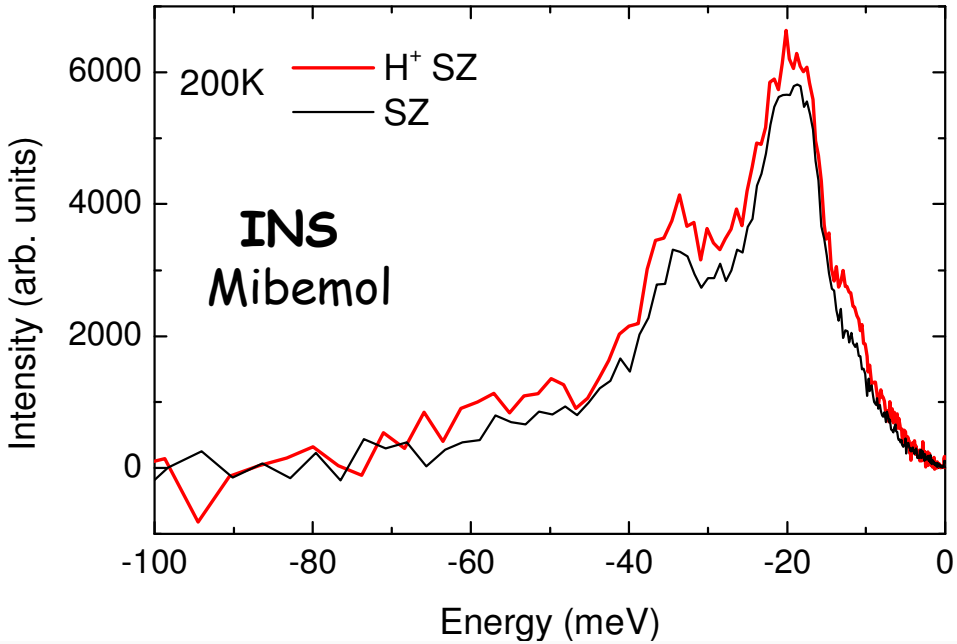


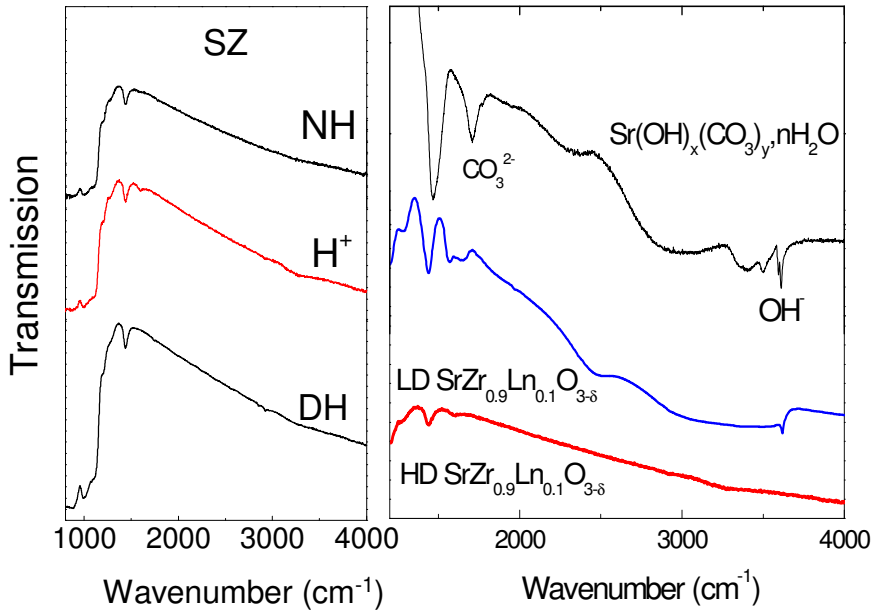


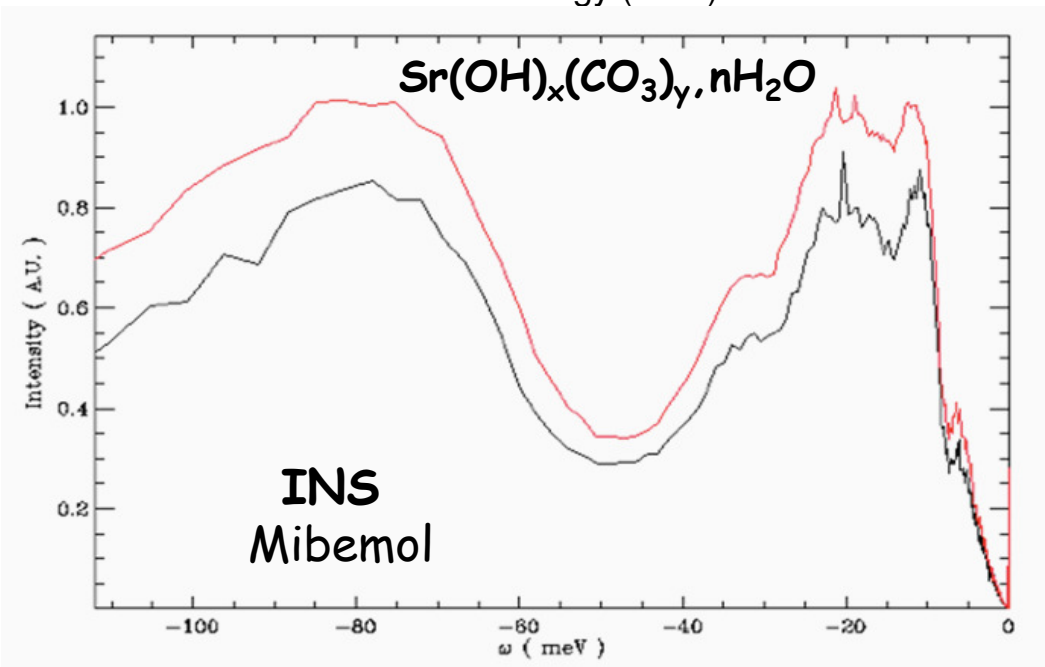
SZ_90% : IR signature due to the surface moieties
SZ_99% : **interstitial proton, free from covalent bonding**

A. Slodczyk et al. MRS Proceedings 1309 (2011)
Ph. Colomban, A. Slodczyk Membranes 2, 493 (2012)
Ph. Colomban, A. Slodczyk J. Raman Spectrosc. (2012) in press

What is a nature of bulk proton? – INS approach



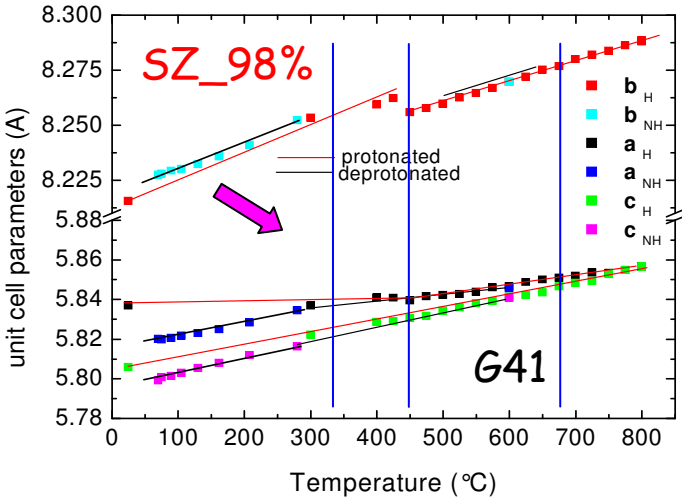




Ph. Colomban, A. Slodczyk
J. Eur. Phys. (2012) in press

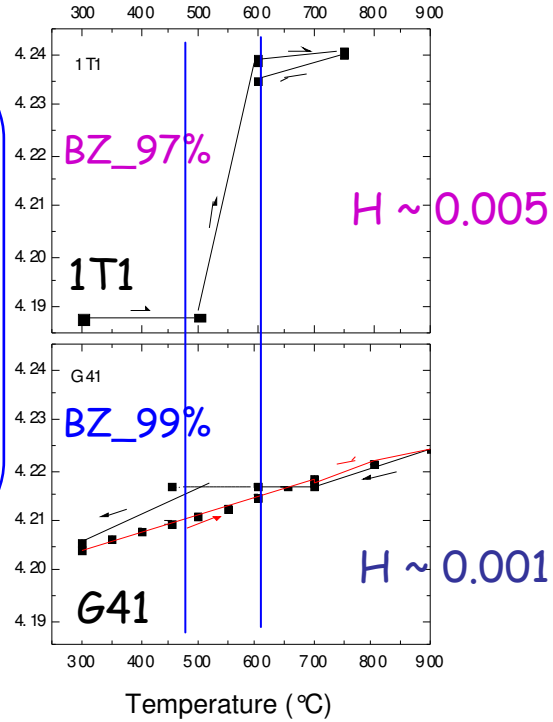
covalent bonding free nature of bulk proton

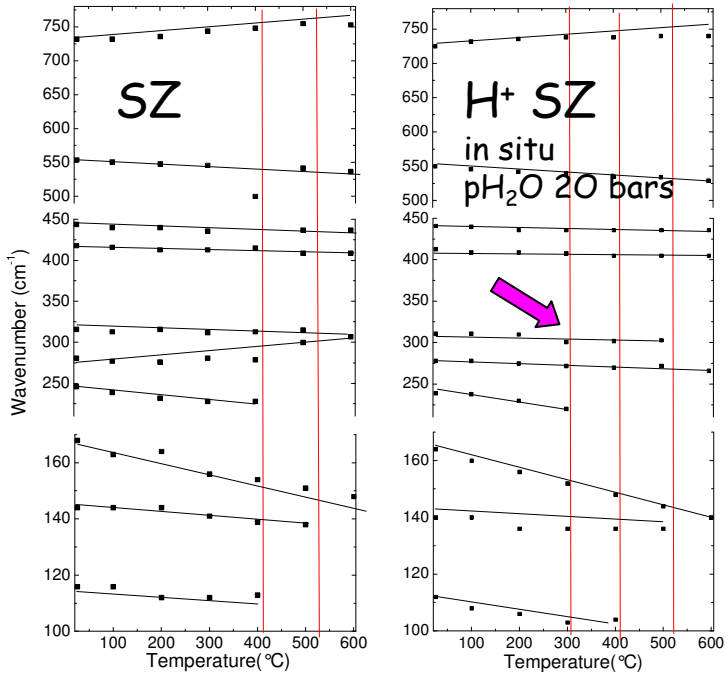
Structural modifications of host perovskite structure



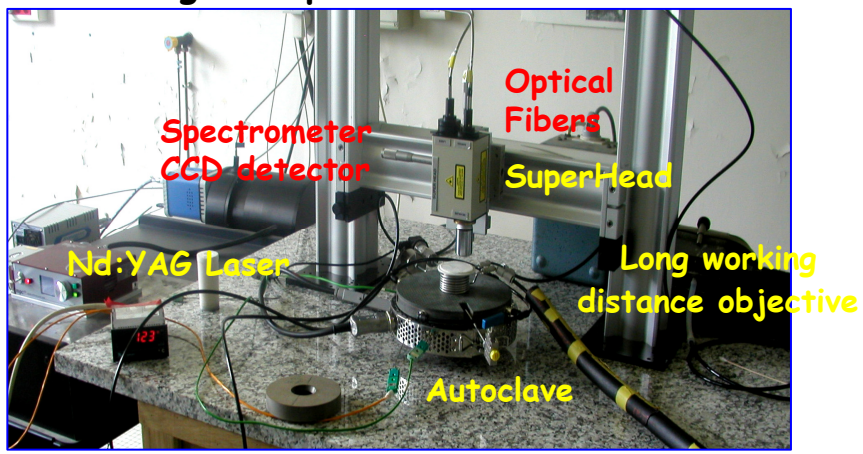
Long range structural modifications in good agreement with the ionic nature of proton!

Structural modifications are proportional to the proton content





High pressure/high temperature Raman *in situ* autoclave

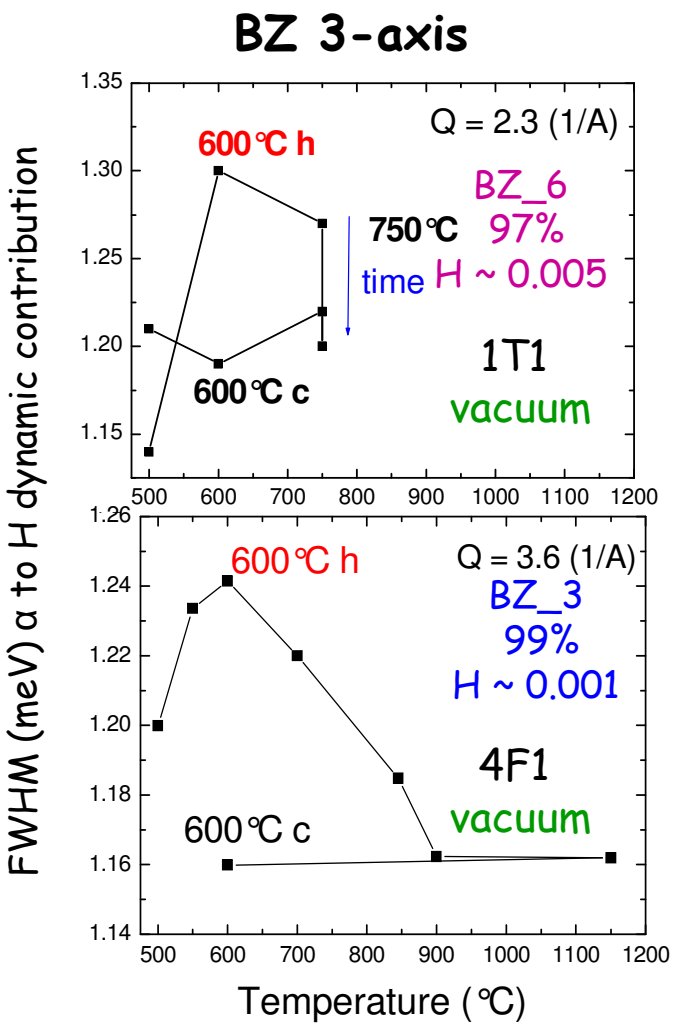


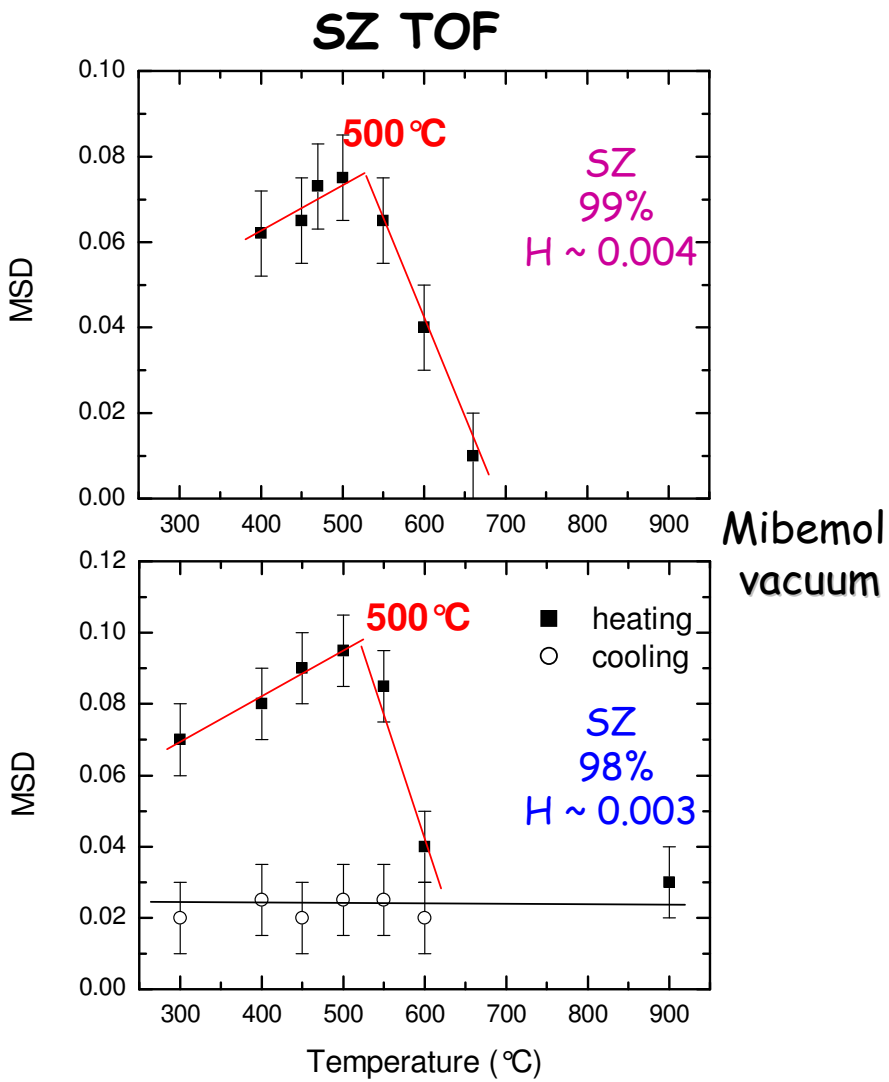
LADIR, Paris FRANCE

Ph. Colomban & A. Slodczyk et al.
Journal of the Physical Society of Japan 79 (2010) 1

A. Slodczyk et al. MRS Proceedings 1385 (2012)

Proton dynamics – QENS results





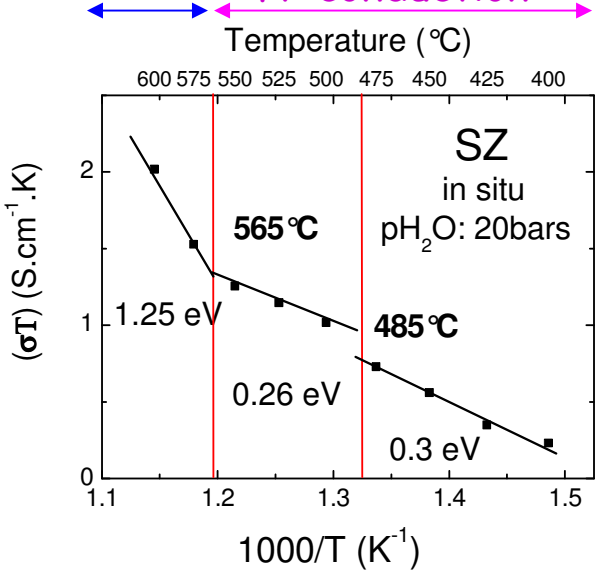
A. Slodczyk et al. J. Mater. Research 27, 1939 (2012)

~450°C -600°C maximal peak broadening or maximal value of MSD
➔ the highest local (meV) proton motion

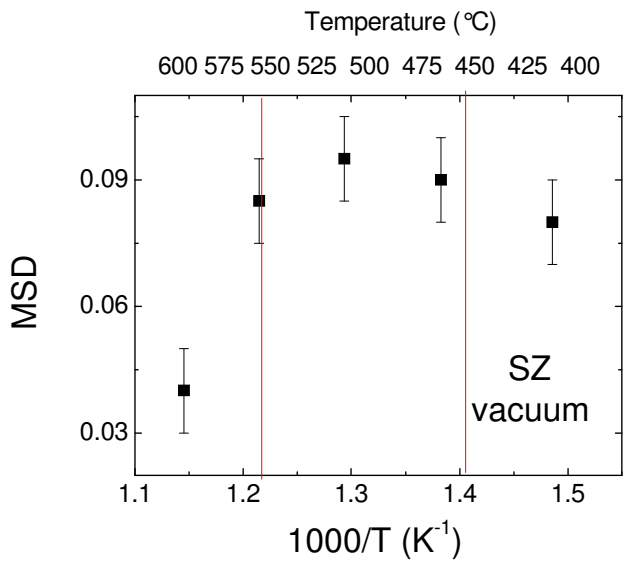
in situ vs. *ex situ*

mixed H^+ / O^{2-} conduction?

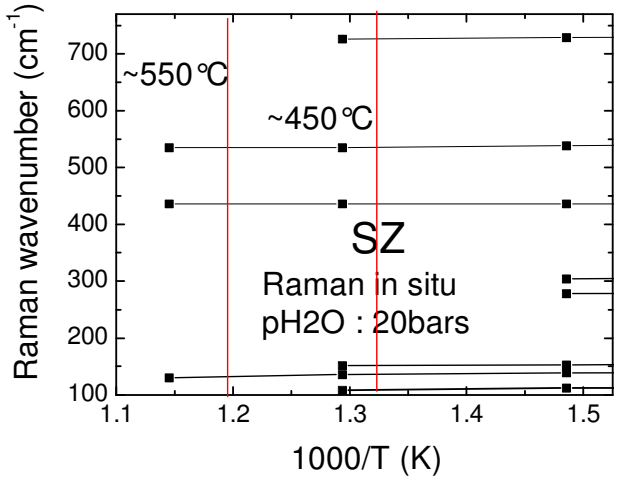
H^+ conduction



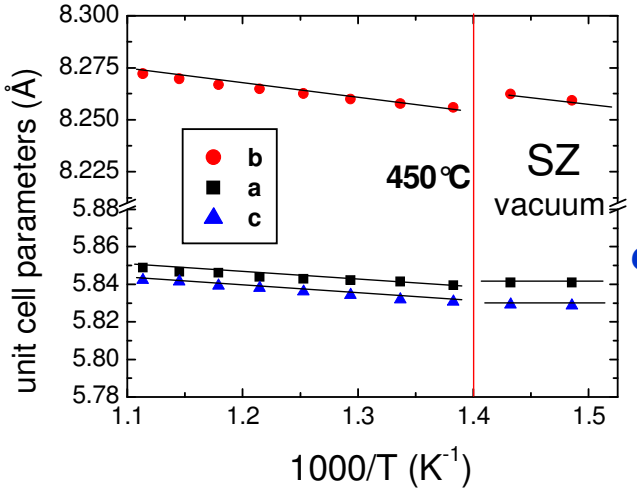
Conductivity electrolyser in situ



QNS ex situ



Raman autoclave in situ



diffraction ex situ

ΔEa ⇔ phase transitions ⇔ local proton dynamics

450-550°C optimum temperature range

Ph. Colomban & A. Slodczyk et al.
Journal of the Physical Society of Japan 79 (2010) 1

Conclusion

- physics and chemistry of Protonics are complex

- differentiation between bulk and surface protonic species is necessary to go further in comprehension of protonic perovskites: « bulk proton doping » : ~ 0.5 10^{-2} mole/mole

- the bulk protons posses the covalent-bond free nature

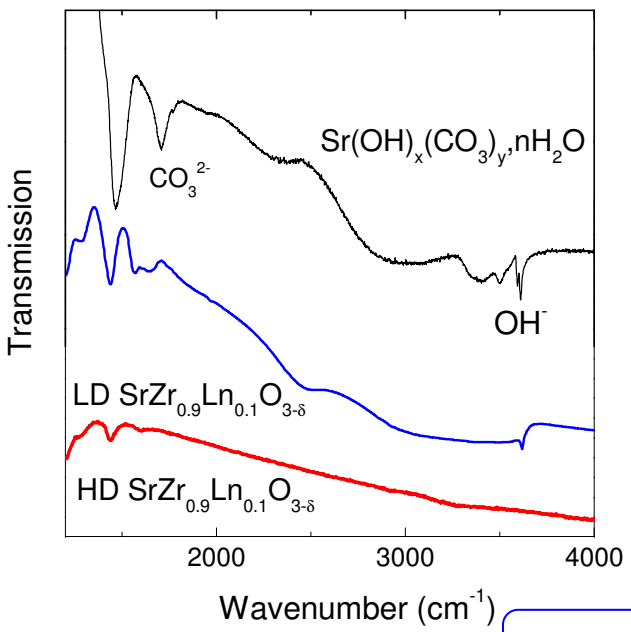
- bulk protons induce long range order structural modifications weak enough to guaranty chemical and mechanical stability

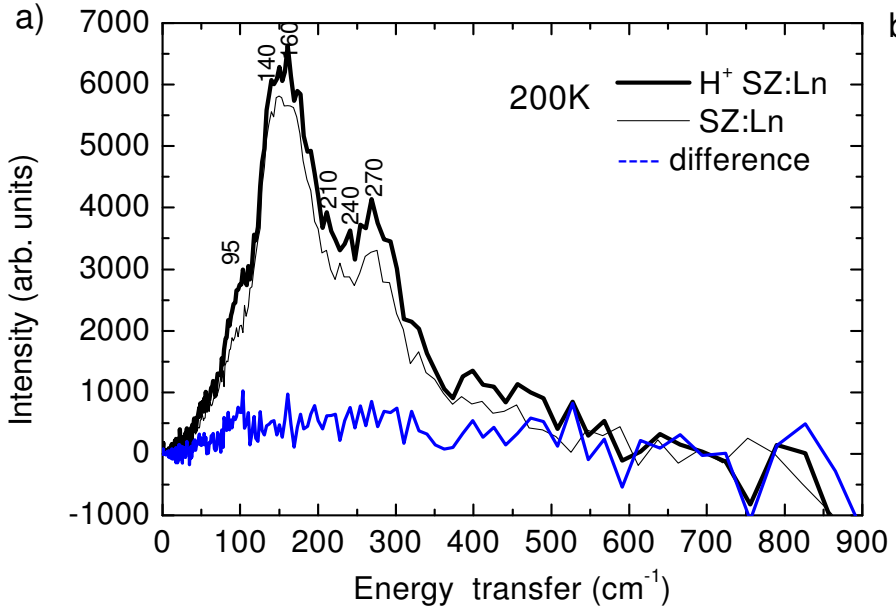
- proton dynamics are complex, correlated to the structural modifications and activation energy changes

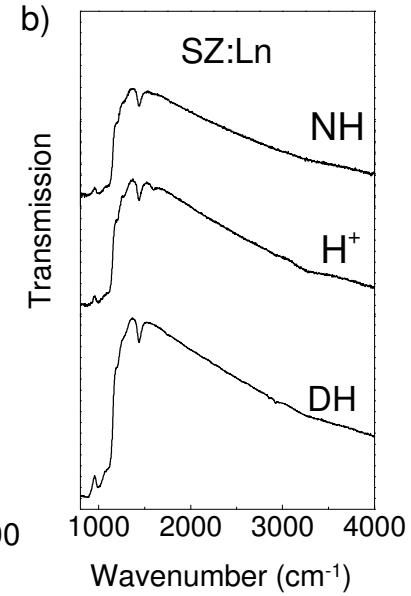
Acknowledgements:

ANR PAN-H CELEVA and H-PAC HELEVA
AREVA-NP, IEM, LISE, SCT, ENS Mines ST-Etienne

What is a nature of bulk proton? – INS approach

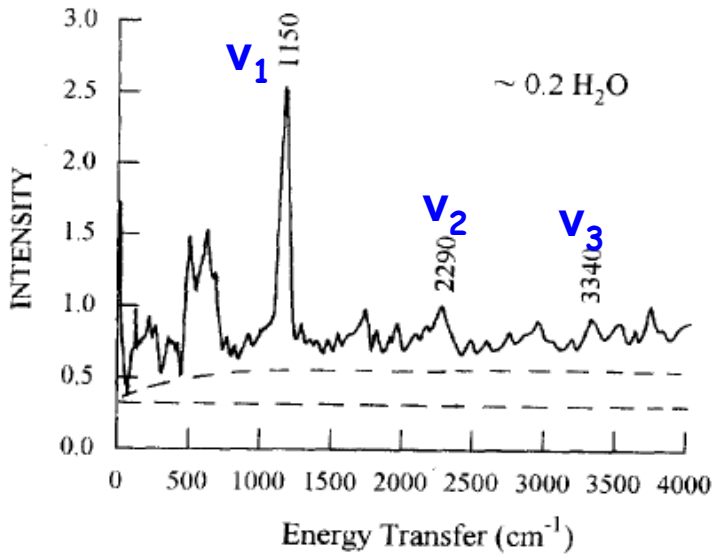






interstitial proton, free from hydrogen bonding

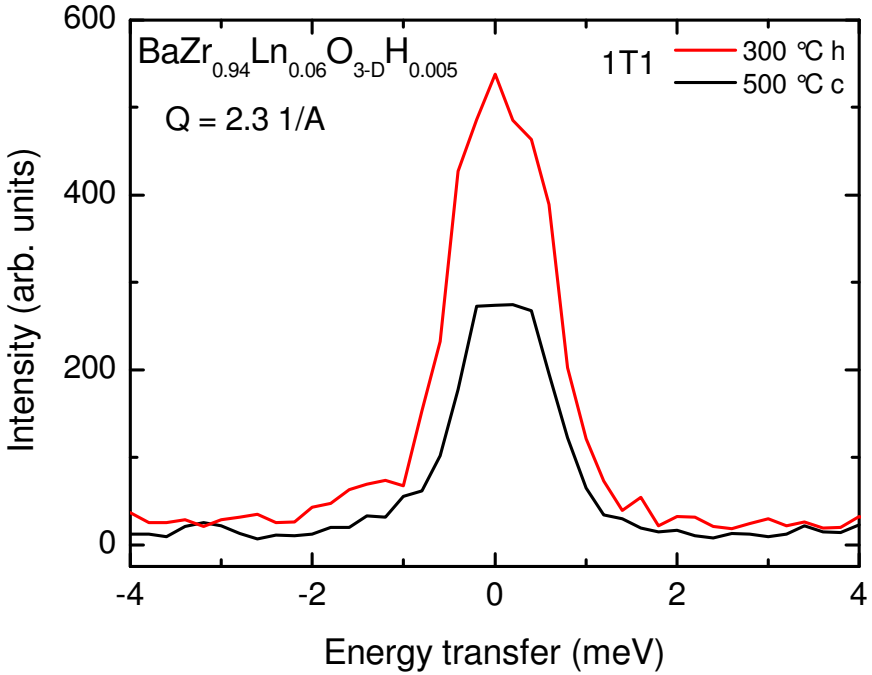
ionic proton ?



gas of proton ?

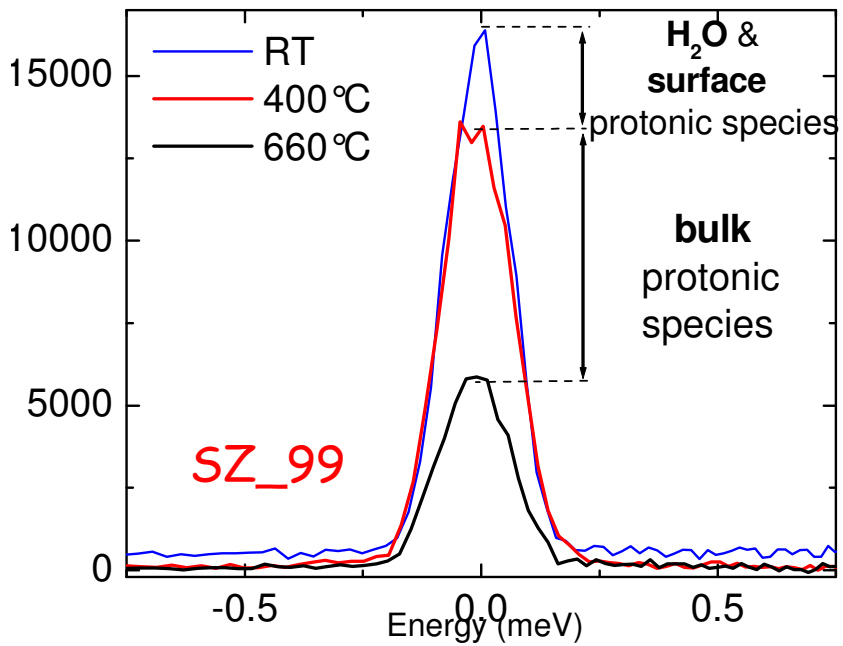
Protonic species content - QENS

3-axis



$BaZr_{0.9}Ln_{0.1}O_{3-\delta}H_z$

TOF

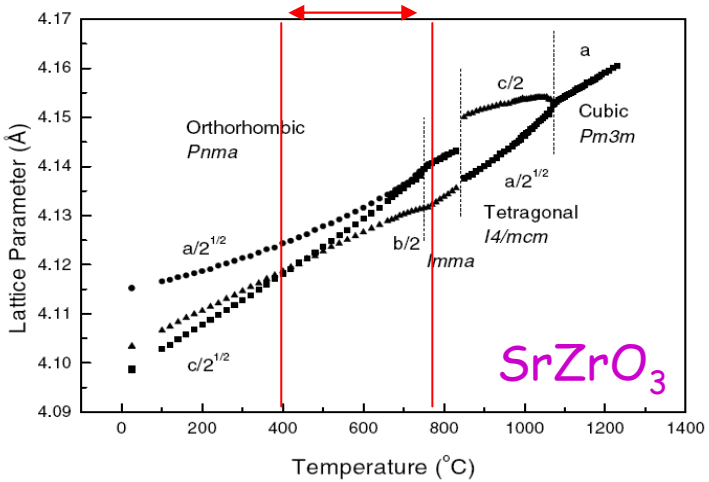


$SrZr_{0.9}Ln_{0.1}O_{3-\delta}H_z$

$$\frac{\sum \sigma_{incoh}(AB_{1-x}Ln_xO_{3-\delta}H_Z)}{\sum \sigma_{incoh}(AB_{1-x}Ln_xO_{3-\delta})} \cong \frac{I_{protonated}}{I_{deprotonated}}$$

Structural studies of host perovskite structure

- thermal and chemical stability
- conductivity mechanism

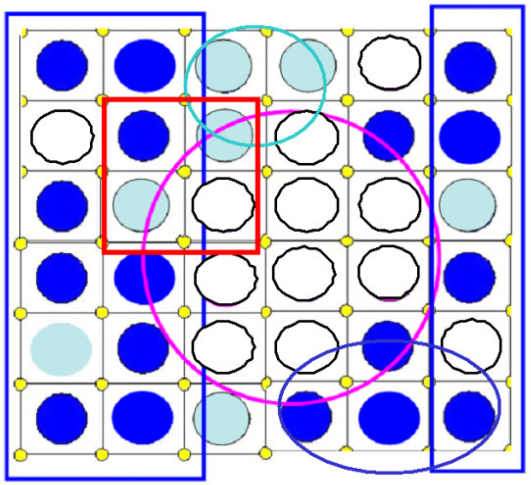


CJ Howard et al.
J. Phys Condens. Matter
2000; 12 L667

reliable diffraction results = ordered materials

Proton conducting perovskite
host structure + Ln/RE substitution ($V_O^{\cdot\cdot}$) + proton doping

➔ non-stoichiometry, local disorder

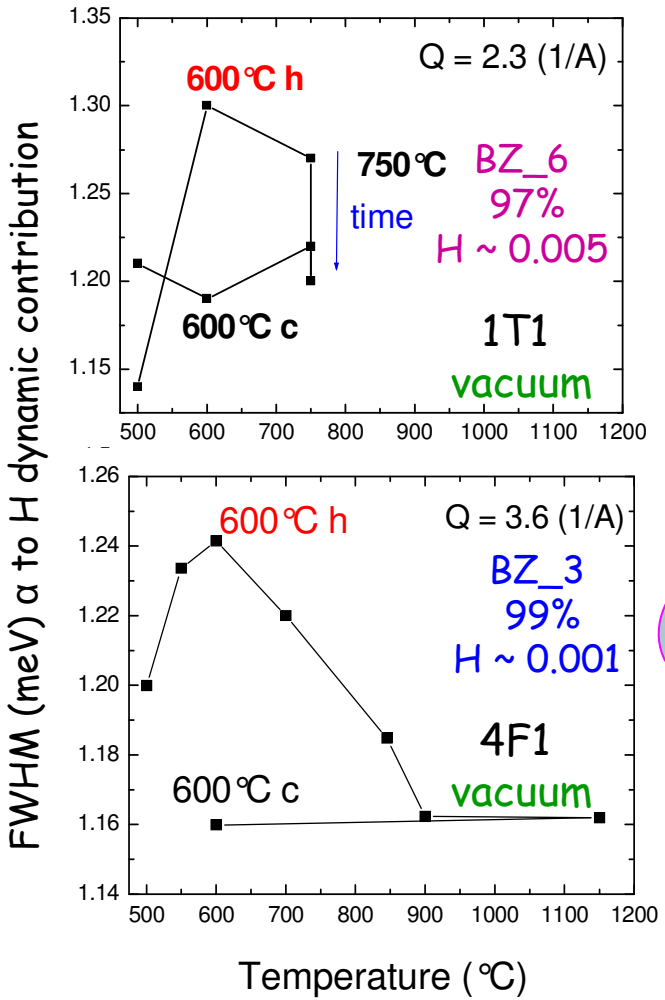


Nanoregions,
distinct local symmetry

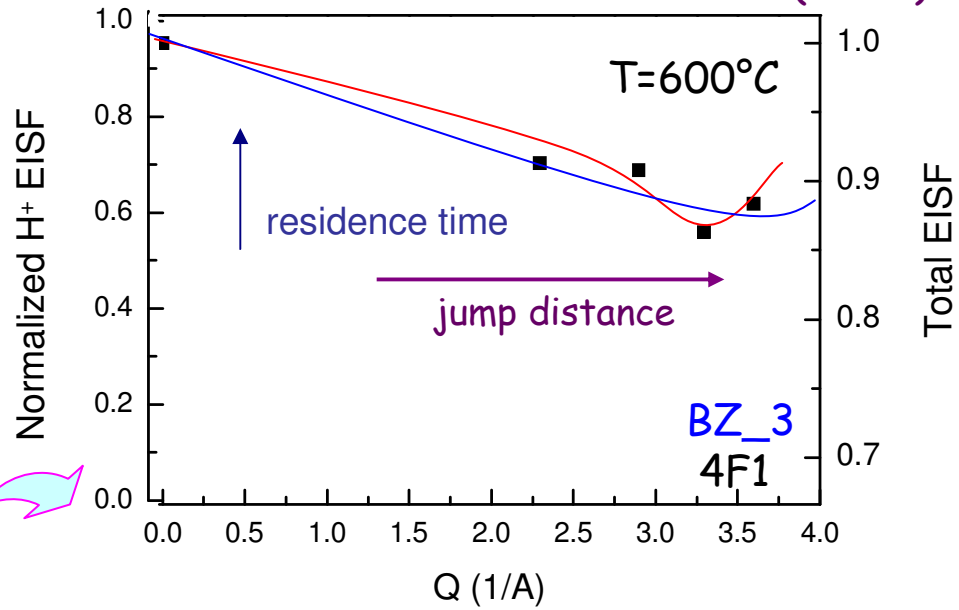
$A(B_{1-x-y}B'_xB''_y)O_{3-d}$
ABO_3
$AB'O_3$
$AB''O_3$

H ???

Proton dynamics – 3 axis results



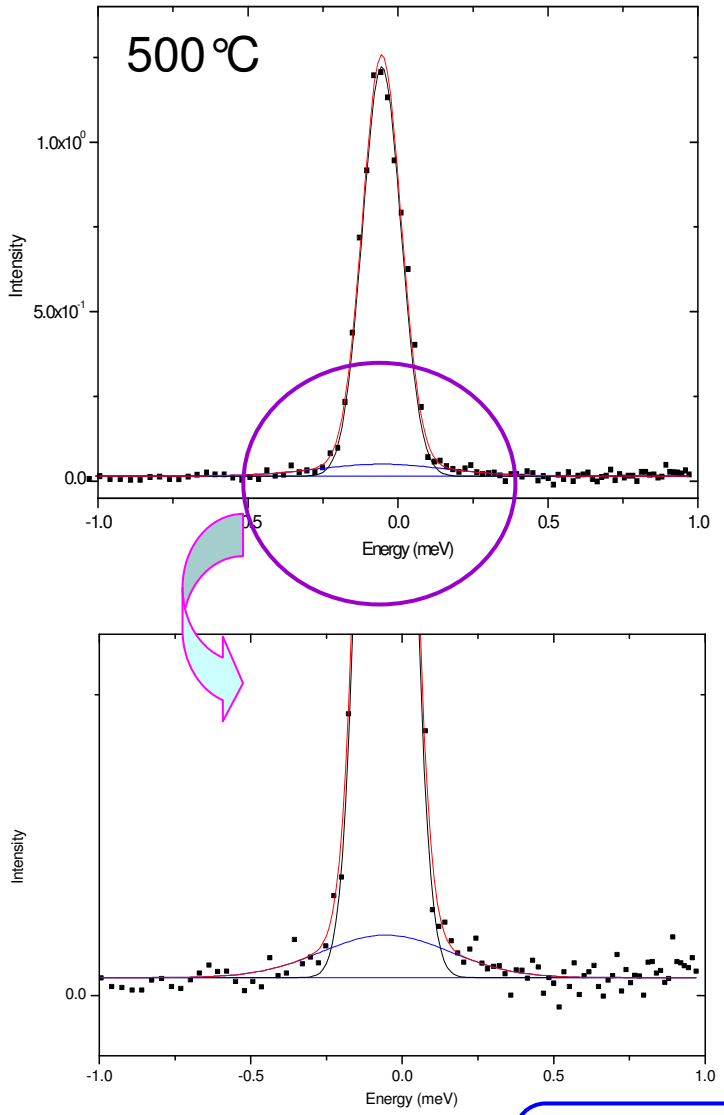
Elastic Incoherent Structure Factor (EISF)

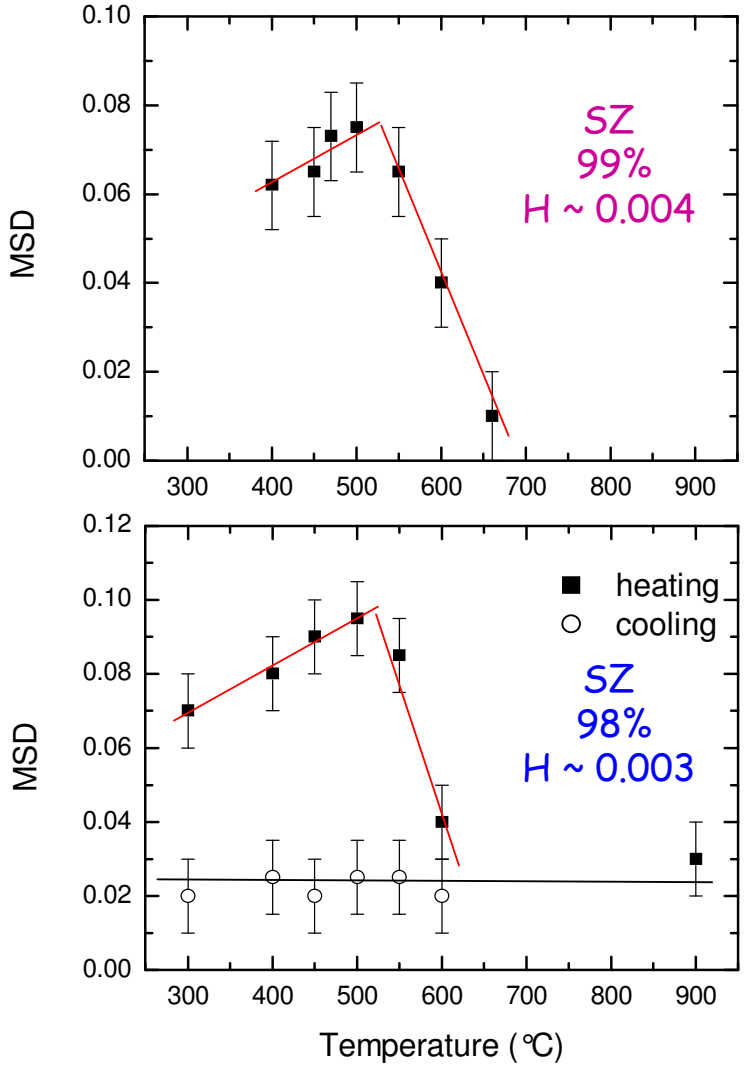


Jumps over n sites ?

~550-600°C maximal peak broadening
the highest local (meV) proton motion

Proton dynamics – TOF results

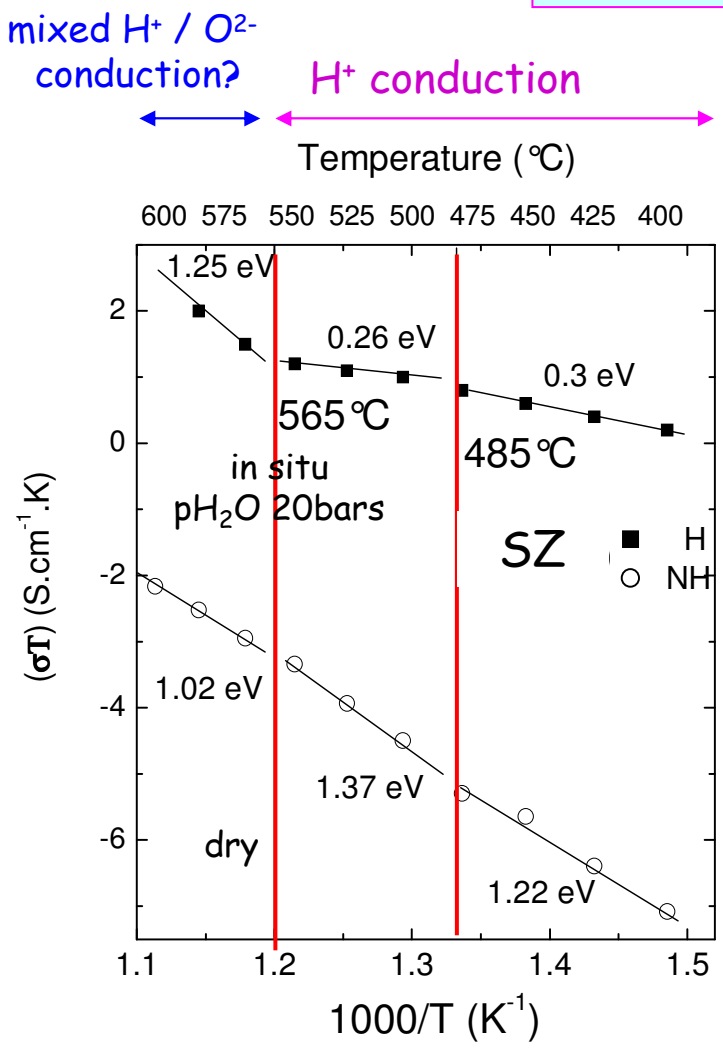




Mibemol
vacuum

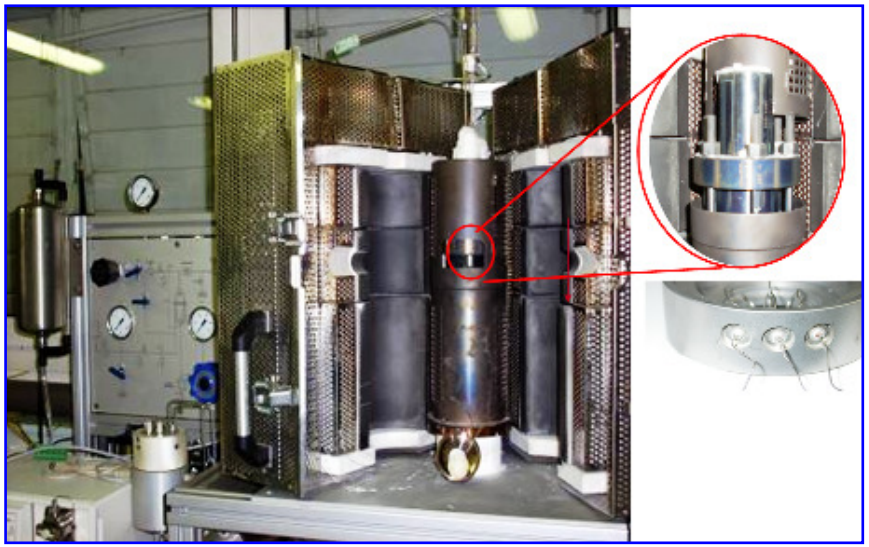
~450- 500°C maximal value of MSD
the highest (meV) proton motion

in situ Conductivity



High pressure/high temperature
Steam Water Electrolyser

(up to 600°C and 50 bars of H_2O)



AREVA NP, Montpellier FRANCE

http://www2.cnrs.fr/presse/comunique/1570.htm

E_a ~ 0.3 eV ➔ Pure proton conduction below 565°C