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

Aneta Slodczyk¹, Philippe Colomban¹,
Daniel Lamago²,³, Gilles André², Natalie Malikova²,
Stephane Longeville², Jean-Marc Zanotti²
Olivier Lacroix⁴ and Beatrice Sala⁴

¹ LADIR UMR 7075 CNRS - UPMC, 75005 Paris, France.
² Laboratoire Léon Brillouin CNRS-CEA, CEA Saclay, 91191 Gif-sur-Yvette, France.
³ Karlsruhe Institute of Technology, IFP, 76021 Karlsruhe, Germany.
⁴ AREVA NP - UM2, Montpellier, 34095, France.
Context

perovskite ceramic

\[ M(\text{Ba, Sr})B(\text{Zr, Ce, Ti})_{1-x}O_{3-\delta}\text{Ln/RE}_yH_z \]

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
Proton size: electron < H<sup>+</sup> < Li<sup>+</sup> ion

The physics and chemistry of proton are unique

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

acceptor covalence shell penetration (OH<sup>-</sup>, H<sub>3</sub>O<sup>+</sup>, NH<sub>4</sub><sup>+</sup>)

weak asymmetric H-bond

strong symmetric H-bond

ionic proton

Extremely complex behaviour of Protonics
High complexity of Protonics ➦ specific methods of analysis

\[
H: \quad \sigma_{\text{incoh}} = 80.26 \text{ barns}; \quad \sigma_{\text{coh}} = 1.76 \text{ barns}
\]

- direct measurement of proton content
- local and long range proton motion, proton dynamics: QENS (meV-\(\mu\)eV)
- 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**

\[(\text{Ba}, \text{Sr})\text{Zr}_{1-x}\text{Ln}_x\text{O}_{3-\delta} H_z\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Density (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaZr(<em>{0.94}\text{Ln}</em>{0.06}\text{O}<em>{3-\delta} H</em>{0.005})</td>
<td>(97%) BZ(_6)</td>
<td></td>
<td>(PCT patent WO 2008/152317 A2 (18-12-2008))</td>
</tr>
<tr>
<td>SrZr(<em>{0.93}\text{Ln}</em>{0.07}\text{O}<em>{3-\delta} H</em>{0.003})</td>
<td>(98%) SZ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaZr(<em>{0.97}\text{Ln}</em>{0.03}\text{O}<em>{3-\delta} H</em>{0.001})</td>
<td>(99%) BZ(_3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrZr(<em>{0.93}\text{Ln}</em>{0.07}\text{O}<em>{3-\delta} H</em>{0.004})</td>
<td>(99%) SZ</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

protonated in autoclaves at high temperature, under high H\(_2\)O vapour pressure

→ water steam electrolysis conditions

Stable electrolytes allowing hydrogen production

AREVA NP, Montpellier FRANCE
Importance of sample processing

$\text{BaZr}_{0.25}\text{In}_{0.75}\text{O}_{3-\delta}$ (cooperation Northern Univ. - Argonne Laboratory)

chemical and mechanical decomposition; premature aging

Idem other Ln-modified perovskites!
Samples and Experiments

**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
Time-of-flight Mibemol Spectrometer

**inelastic neutron scattering:** Time-of-flight Mibemol Spectrometer

**neutronography**

**high dense (97-99%) ceramics stable in operating conditions**
(Ba,Sr)Zr$_{1-x}$Ln$_x$O$_{3-\delta}$ Hz

(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
- Time-of-flight Mibemol Spectrometer

**inelastic neutron scattering**

- Time-of-flight Mibemol Spectrometer

**neutronography**

**Samples and Experiments**

**high dense (97-99%) ceramics stable in operating conditions**
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- **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
  - Time-of-flight Mibemol Spectrometer

- **inelastic neutron scattering**
  - Time-of-flight Mibemol Spectrometer

**neutronography**

**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$_2$O)

**in situ Conductivity**
  - water steam electrolyser (20-600°C, 20 bars H$_2$O)
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

- **Bulk** protonic species
- **Surface** protonic species

**Energy (meV)**

**Intensity (arb. units)**

- **HD 99%**
- **SZ**
- **TOF**

**1T1 300 °C h**

**Q = 2.3 1/A**

**BZ 3-axis**

**Sr(Zr, Ln)O$_3$-δ**

**TGA**

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

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

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

Protonic species content

Protonic species content


neutronography

SZ (250°C/40bar/72h)  
surface protonic species

Ph. Colomban, A. Slodczyk Membranes 2, 493 (2012)
What is a nature of bulk proton? - TGA and IR approach

**SZ_99%** \(\rightarrow\) \(500^\circ\text{C}/80\text{ bar}/5\text{ days} \rightarrow \text{bulk protons}

**SZ_90%** \(\rightarrow\) \(200^\circ\text{C}/15\text{ bar}/5\text{ days} \rightarrow \text{surface protonic species + traces of bulk protons}

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**SZ_90%**: IR signature due to the surface moieties

**SZ_99%**: interstitial proton, free from covalent bonding

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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
Structural modifications of host perovskite structure

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

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

A. Slodczyk et al. MRS Proceedings 1385 (2012)
Proton dynamics - QENS results

BZ 3-axis

FWHM (meV) a to H dynamic contribution

Temperature (°C)

Q = 2.3 (1/A)

600°C h

75°C 97%
time H ~ 0.005

1T1 vacuum

600°C c

Q = 3.6 (1/A)

BZ_6

99%

600°C c

1T1 vacuum

MSD

SZ TOF

~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

Temperature (°C)

Conductivity electrolyser

in situ

Raman in situ

in situ

QNS ex situ

MSD

450-550°C optimum temperature range

$\Delta E_a \Leftrightarrow$ phase transitions $\Leftrightarrow$ local proton dynamics

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

![Graph 3-axis](Graph_3-axis.png)

TOF

![Graph TOF](Graph_TOF.png)

\[ \sum \sigma_{\text{incoh}}(AB_{1-x}Ln_xO_{3-\delta}H_z) \approx \frac{I_{\text{protonated}}}{I_{\text{deprotonated}}} \]

\[ \text{BaZr}_{0.9}\text{Ln}_{0.1}\text{O}_{3-\delta}\text{H}_z \]

\[ \text{SrZr}_{0.9}\text{Ln}_{0.1}\text{O}_{3-\delta}\text{H}_z \]
Structural studies of host perovskite structure

- thermal and chemical stability
- conductivity mechanism

Reliable diffraction results = ordered materials

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

$\Rightarrow$ non-stoichiometry, local disorder

CJ Howard et al.
Proton dynamics - 3 axis results

- 600°C h
- 750°C BZ_6
- BZ_3
- 97%
- 99%
- H ~ 0.005
- H ~ 0.001

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

Elastic Incoherent Structure Factor (EISF)

- Normalized H⁺ EISF
- Jumps over n sites?
- residence time
- jump distance

Temperature (°C)

FWHM (meV) α to H dynamic contribution

T=600°C

BZ_3 4F1

BZ_6

Normalized H⁺ EISF

Q (1/A)

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0

0.7 0.8 0.9 1.0

Total EISF

Normalized H⁺ EISF

Q (1/A)

0.0 0.2 0.4 0.6 0.8 1.0

0.7 0.8 0.9 1.0
Proton dynamics - TOF results

500°C

- Intensity vs. Energy (meV)
- MSD vs. Temperature (°C)

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

Mibemol vacuum

SZ 99%
H ~ 0.004

SZ 98%
H ~ 0.003
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 \sim 0.3 \text{ eV} \Rightarrow \text{Pure proton conduction below 565°C}