ATOMIC SCALE PICTURE OF THE PROTON CONDUCTION MECHANISM IN THE TETRAHEDRAL NETWORK OF LA$_{1-x}$

$_x$BA$_{1+x}$GAO$_{4-x/2}$

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$\text{LA}_{1-x}\text{BA}_{1+x}\text{GAO}_{4-x/2}$

- a system with tetrahedral ($\text{GaO}_4$) units
- increasing the barium content in expense of lanthanum content leads to oxygen vacancies for charge compensation.
- water can be incorporated into the oxygen vacancies as protonic defects from humid atmospheres
- exhibits oxide ion conduction in dry atmospheres, and proton conduction in humid atmospheres

- DFT and MD [1] suggest inter-tetrahedron proton transfer to be the rate limiting process

SAMPLE PREPARATION LA$_{0.8}$BA$_{1.2}$GAO$_{3.9}$ AND XRPD

- Syntheses at 1400 °C
- Refinements show unusual ADP for oxygen in the vicinity of the Ba
- Neutron diffraction essential to have accuracy on oxygen positions/occupations. X-ray not sensitive enough to have accurate results.
TG AND IMPEDANCE SPECTROSCOPY

- Hydration ratio
  \[ \text{La}_{0.8}\text{Ba}_{1.2}\text{GaO}_{3.9}\times0.08\text{H}_2\text{O} \]

- Activation energy for proton conduction ca. 0.77 eV [2]

NPD OF $\text{La}_{0.8}\text{Ba}_{1.2}\text{GaO}_{3.9}$

TOF-NPD @ POWGEN (SNS) @ 300K using two different center wavelengths (CWLs)

- 1.066 Å (d-spacing from 0.29 Å to 3.09 Å) for accurate nuclear structure and ADPs
- 3.731 Å (d-spacing from 1.65 Å to 8.24 Å) additional nuclear reflections if further ordering occurs

Orthorhombic structure
Space group $\text{P}_{2\frac{1}{2}2\frac{1}{2}2\frac{1}{2}}$

$a = 10.078(5)$ Å
$b = 7.336(4)$ Å
$c = 5.936(4)$ Å

Oxygen vacancies are carried by $\frac{1}{4}$ of the sites and “travel” along the $c$ axis direction. Locally $\text{Ga}_2\text{O}_7$ entities are created implying a rocking motion of two other oxygen atoms.
NPD OF LA$_{0.8}$BA$_{1.2}$GAO$_{3.9} \times 0.08$D$_2$O

The inclusion of D$_2$O shows an increase of the volume and some residues associated with D sites are observable along the path shown by dashed lines.

Oxygen from water is partially filling the vacancies.
Proton are traveling through the “rocking” oxygen atoms.
QENS MEASUREMENTS

• Proton diffusion in $\text{La}_{0.8}\text{Ba}_{1.2}\text{GaO}_{3.9}\times0.08\text{H}_2\text{O}$ measured @ BASIS backscattering spectrometer @ SNS
  • High energy resolution 3 $\mu$eV
  • Residence times measurable from 1 ps to 1 ns
  • Length scales measurable from 3 Å to 30 Å
TYPICAL QENS SPECTRA

\[ S(Q, \omega) = p_1 \delta(\omega) + p_2 \frac{1}{\pi} \frac{\Delta(Q)}{\omega^2 + \Delta^2} + B \]
QENS SPECTRA

- QENS spectra were measured at various temperatures from 30 to 500 K.
- Hydrated sample measured to determined the atomic scale proton diffusion process
- Dry sample measured for comparison
- Data fitted with model containing two Lorentzian functions – each one associated with a particular dynamical process of the protons in the sample

Fit example at 466 K at 1.3 Å⁻¹
FAST LOCALIZED PROCESS

The width of the broad Lorentzian component is “constant” as a function of Q, indicating localized proton motion.

- Activation energy of 70 meV
- Corresponds to the literature value for the inter-tetrahedron proton transfer [1]

SLOW PROCESS

- The Q dependency of the HWHM of the narrow Lorentzian component indicates long range translational diffusion of protons
- Activation energy for translational diffusion of protons is 0.5 eV

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Diffusion coefficients and residence times for translational diffusion
CONCLUSIONS:

- Long range translational diffusion of protons over more than 3 unit cells was observed by QENS, $E_a = 0.5$ eV.

- Localized proton diffusion was observed, $E_a = 0.07$ eV.

- Deviation from the localized and translational diffusion was observed at $Q = 1.5 \, \text{Å}^{-1}$, indicating a faster process on a distance of about 4.2 Å.
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Beamtime:
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FRM2