Proton dynamics in barium zirconates investigated with quasielastic neutron scattering

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Next-generation neutrons and x-rays to appear in Sweden

The European Spallation Source (ESS)

• Next-generation neutron facility, in operation around 2020.

The MAX IV synchrotron radiation facility

• Next-generation synchrotron source (MAX IV) close by, in operation by 2015.
Proton dynamics in barium zirconates investigated with quasielastic neutron scattering

Proton dynamics

1. Vibrational motions, O-H stretches and wags, (fs)
2. Local diffusional motions (ps)
3. Long-range translational diffusion (ns)

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Quasielastic neutron scattering (QENS)

Time-space domain covered by different QENS methods
Quasielastic neutron scattering (QENS)

Neutron scattering in the simple picture

- Scattered intensity as a function of scattering angle (diffraction) gives structural information.

- Energy change gives information about dynamics in the material (in- or quasielastic scattering).
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\[ S(Q, \omega) \]

\[ \omega = E_0 - E_1 \]
Neutron scattering in the simple picture

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QENS on 10% Y- and Sc-doped BaZrO$_3$

Bulk proton mobility in BaZr$_{0.9}M_{0.1}$O$_3$ ($M = Y, In, Gd, Sc$), derived from conductivity exp. (Replotted from Kreuer et al., SSI 145 (2001) 295)

Fact:
- Strong variation in the proton diffusivity, although the average crystal structure the same (cubic).

Question:
- Is there any difference in the proton dynamics on the short length-scale (1—5 Å), probed by QENS, that can explain the difference in proton mobility on the longer length-scale derived from conductivity experiments.
QENS on 10% Y- and Sc-doped BaZrO$_3$

QENS spectra at different temperatures
(data from the IN6 TOF-spectrometer, ILL)

$Q = 1.9 \text{ Å}^{-1}$

10Y:BZO

$S_{\text{meas}}(Q, \omega)$

Quasielastic part

Resolution function

$T = 495 \text{ K}$

$T = 465 \text{ K}$

$T = 430 \text{ K}$

10Sc:BZO

$S_{\text{meas}}(Q, \omega)$

Quasielastic part

Resolution function

$T = 495 \text{ K}$

$T = 465 \text{ K}$

$T = 430 \text{ K}$

The total mean square displacement $<u^2>$, derived from the $S(Q, \omega)$ spectra

$e^{-<u^2> Q^2} = \frac{S_{\text{meas}}(Q, \omega = 0)}{\int_{-2}^{+2} S_{\text{meas}}(Q, \omega) d\omega}$

- The $T$-dependence of $<u^2>$ suggests we pick up dynamics, other than vibrational motions, at $T \approx 300 \text{ K}$ and above.
**QENS on 10% Y- and Sc-doped BaZrO$_3$**

**Quasielastic widths vs. $Q$ (widths at different temperature separated by 0.1 meV)**

- **The proton motion is local** (since $Q$-independent) and has a characteristic time-scale of $\tau \approx 4$ ps (Y) and 6 ps (Sc) ($\tau = h/\Delta \omega$).

- **Very small activation energies:**
  - $E_a = 10$ meV (10Y:BZO) and $E_a = 30$ meV (10Sc:BZO).
  - Compare to $E_a$[Conductivity] $\approx 500$ meV.
Fitting to the $Q$-dependence of the quasielastic intensities

- **Jump diffusion models**
  - Over two sites (proton transfer process)
  - Over four sites (rotational motion of the $–$OH group; in a simple picture, there are four proton sites around each oxygen).

- **Problem**: impossible to discern the two models from each other, from the experimental data alone. Measurements to larger $Q$-values needed.

- **Comparison with jump distances and activation energy obtained from DFT calculations**
  - Would suggest proton transfer close to dopant atom (T11), for both materials.

NSE case study on \( \text{BaZr}_{1-x} \text{In}_x \text{O}_{3-x/2} \) \((x = 0.10 \text{ and } 0.50)\)

Time-space domain covered by different neutron methods

Neutron spin-echo (NSE) spectroscopy

- Large accessible time-range (ps—ns); covers both local and long-range dynamics.
- Intermediate scattering function: \( I(Q,t) \)

\[
I(Q,t) = \text{FT}[g(r,t)]
\]
**NSE case study on BaZr$_{1-x}$In$_x$O$_{3-x/2}$ ($x = 0.10$ and $0.50$)**

**$I(Q,t)$ at $T = 500$ K and $Q = 1.05$ Å$^{-1}$**

- *Data from the IN11 spectrometer at ILL*
  - $T$-range: 470—525 K
  - $Q$-range: 0.83—1.26 Å$^{-1}$ ($r \sim 5—7.5$ Å)
  - $t$-range: 5 ps—1.3 ns

**$I(Q,t)$**

- $x = 0.10$
  
  
  $I(Q,t) = e^{-t/\tau} + 0.32$, where $\tau \sim 60$ ps

- $x = 0.50$
  
  
  $I(Q,t) = e^{(-t/\tau)^\beta}$ $\beta \sim 0.50$, $<\tau> \sim 1$ ns, $E_a = 0.75$ eV

- The NSE data suggests local process for $x = 0.10$, with a well defined time scale.

- For $x = 0.50$, a wide distribution of diffusional rates is observed. $E_a = 0.75$ eV (high?).

**Further data analysis in progress**
Dopant induced local structural distortions revealed by Raman spectroscopy

- The presence, and growth, of Raman bands suggest the presence of local distortions of the average cubic structure. The Raman spectrum of a “perfectly” cubic perovskite is featureless.

- Structure goes from perovskite-like ($x = 0—0.75$) to brownmillerite-like ($x > 0.75$) with increasing $x$. 

Karlsson et al., Chem. Mater. 20 (2008) 3480
Dehydrated samples: Raman spectra essentially the same. Small structural differences.

Hydrated samples: Raman spectra dissimilar. Larger structural differences.

“Proton configurations”: more well defined for un- and Ga-doped materials, than for Sc- and Y-doped.

For more about this, see Poster #13 (Thursday), Bielecki et al.
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- Johan Bielecki (Dept. Applied Physics, Chalmers) – (Raman spectroscopy)

Experiments:
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- Chalmers, Dept. Applied Physics [Raman spectroscopy]

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References:
- M. Karlsson, “Perspectives of neutron scattering on proton conducting oxides” (To appear in Dalton Trans.)

Thank you for your attention!
Neutron scattering

Scattering geometry

\[ k = \frac{2\pi}{\lambda} \]

\[ Q = k_0 - k_1 \]

\[ E = \frac{(\hbar k)^2}{2m_n} \]

\[ \Delta E = \hbar \omega = E_0 - E_1 \]
Neutron spin-echo results: In-doped BaZrO$_3$ ($x = 0.50$)

**Stretching parameter**

\[
\beta = 0.39 \quad T = 470 \text{ K}
\]

\[
\beta = 0.42 \quad T = 500 \text{ K}
\]

\[
\beta = 0.47 \quad T = 525 \text{ K}
\]

**Effective diffusion coefficient**

\[\frac{1}{\langle \tau \rangle} = D \cdot Q^2\]

**Average relaxation rate**

\[I(Q, t) = e^{(-t/\tau)^\beta}\]

\[\langle \tau(Q) \rangle = \frac{\tau(Q)}{\beta} \Gamma[1/\beta(Q)]\]

\[\frac{1}{\langle \tau \rangle} = D \cdot Q^2\]

\[\ln[D(\AA^2 \text{ns}^{-1})] = \frac{E_a}{1000T (\text{K}^{-1})} - 1.5\]

\[E_a = 0.75 \text{ eV}\]