Experimental report

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Proposal: 7-03-168 **Council:** 4/2017

Title: Study of H-diffusion mechanism in BaCe0.4Zr0.4Y0.2O3-d; proton conducting perovskite

Research area: Materials

This proposal is a new proposal

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Samples: BaCe0.4Zr0.4Y0.2O3-d

Instrument	Requested days	Allocated days	From	To
IN16B	3	2	03/07/2018	05/07/2018
IN5	2	0		

Abstract:

BaZrO3 and BaCeO3-based materials have potential application as electrolytes for solid oxide fuel cells (SOFCs) and solid oxide electrolizer cells (SOECs) due to lower operating temperatures and higher efficiencies with respect to commercial electrolytes (CGO, LSGM, YSZ). Also, these materials have been proposed as isotopic separation membranes and water sensors. The understanding of protonic defect mobilities and lattice distortions are crucial to develop materials with high protonic conduction.
Thus, information about proton diffusion coefficient and average proton jumping length, by QENS under wet (H2O vapour) and dry atmospheres for the BaCe0.4Zr0.4Y0.2O3-d perovskite would help us to understand proton dynamics, between 298 and 1073 K. The combination of H-dynamics with in situ structural determinations would give us insights about diffusion mechanism of protons and how it is affected by structural changes. We will compare this information with EIS measurements in order to separate H-ion from O-ion transport.

Study of H-diffusion mechanism in $BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ proton conducting Perovskite

Experimental Report: Proposal 7-03-168

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Instrument: IN16B

Dates: July 3 and 4, 2018

Instrument Responsible: Bernhard Frick

Abstract

$BaZrO_3$ and $BaCeO_3$-based materials have potential application as electrolytes for Solid Oxide Fuel Cells (SOFCs) and Solid Oxide Electrolyzer Cells (SOECs) due to lower operating temperatures and higher efficiencies with respect to commercial electrolytes (CGO, LSGM, YSZ). Also, these materials have been proposed as isotopic separation membranes and water sensors. The understanding of protonic defect mobilities and lattice distortions are crucial to develop materials with high protonic conduction. Thus, information about proton diffusion coefficient and average proton jumping length, by Quasielastic Neutron Scattering (QENS) under wet (H_2O vapor) and dry atmospheres for the $BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ perovskite would help us to understand proton dynamics, between 25 and 800 ºC. The combination of H-dynamics with in situ structural determinations would give us insights about diffusion mechanism of protons and how it is affected by structural changes.

Experimental report

$BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ (BCZY) perovskite was synthesized by Solid State Reaction (SSR) and sintered at 1600 °C for 12 hours. Sintered pellets were grinded in mortar when powders were required. Phase purity was checked by laboratory X-Ray Diffraction (XRD) using a PANalytical Empyrean diffractometer with Cu K_α radiation, graphite monochromator and PIXcel^{3D} detector.

QENS spectra of BCZY were collected while heating between room temperature and 800 ºC under atmospheric air flow. Spectra were collected at IN16B with an incident wavelength of 6.271 Å and Si (111) unpolished analyzer. The energy resolution is ~ 0.75 μeV and maximum momentum transference ($Q = \frac{4\pi}{\lambda}\sin\theta$) of 1.9 Å^{-1}. The spectra were collected by using the high flux (HF) standard position.

The sample was put inside quartz tubes that fit the IN16B furnace which operates under vacuum. A capillary connecting the tubes with an external pump allowed us to keep the sample under an air flow at atmospheric pressure (see Figure 1). To ensure sample hydration, the BCZY powder was annealed into the quartz tube at 400 °C for 2 hours under wet air before starting the measurements. Then it was cooled down and a QENS spectrum was collected at room temperature, before starting to heat up to 800°C, stopping regularly to make QENS acquisitions at 25, 100, 200, 300, 400, 500, 600, 700 and 800 ºC. Additionally during each heating step, the intensity in the elastic channel at $\hbar\omega = 0$ (elastic fixed window scan EFWS) and inelastic channel $\hbar\omega = 2\ \mu eV$ (inelastic fixed window scan IFWS) were also collected.

The data have been corrected using LAMP in order to obtain the dynamic structure factor $S(Q, \hbar\omega)$ at each temperature within the dynamic range of 30 μeV. For the analysis, detectors heavily "contaminated" by coherent scattering corresponding to Bragg reflections were discarded. For the others, the signal is dominated by the incoherent scattering from the water hydrogens and the $S(Q, \hbar\omega)$ data were fitted using a model consisting of a delta function plus the Chudley-Elliot Model (CEM) for jump diffusion. This model consists of a single Lorentzian function of half-width at half-maximum (HWHM), $\Gamma/2$:

$$\frac{\Gamma}{2} = \frac{\hbar}{\tau}\left(1 - \frac{\sin(Ql)}{Ql}\right) \quad (1)$$

where l is the characteristic jump length and τ the mean residence time. Both parameters can then be used to determine a diffusion coefficient D_H for water in BCZY, as:

$$D_H = \frac{l^2}{6\tau} \quad (2)$$

Table 1 presents the results of fits from QENS spectra by using CEM. Fitting the results obtained between 300 and 600 °C by Arrhenius law, one obtains a value of τ_0 = 2.2 ± 1 ps and E_a = 24 ± 6 kJ/mol.

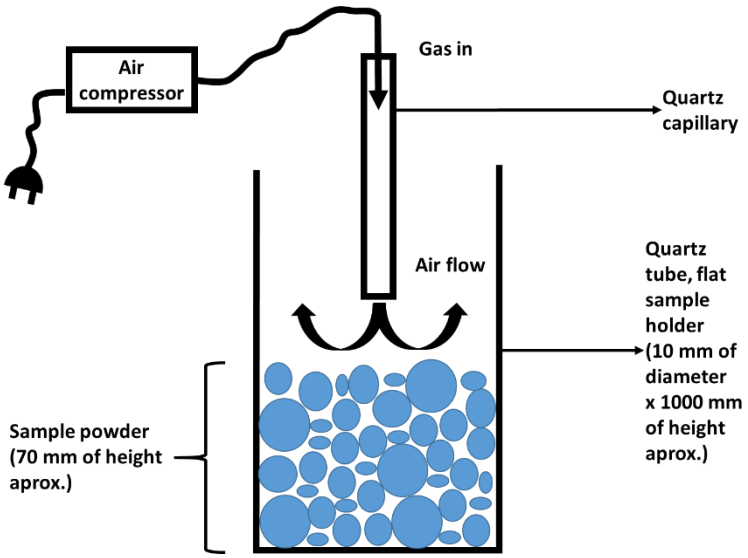

Figure 1. Experimental setup for QENS measurements under wet air

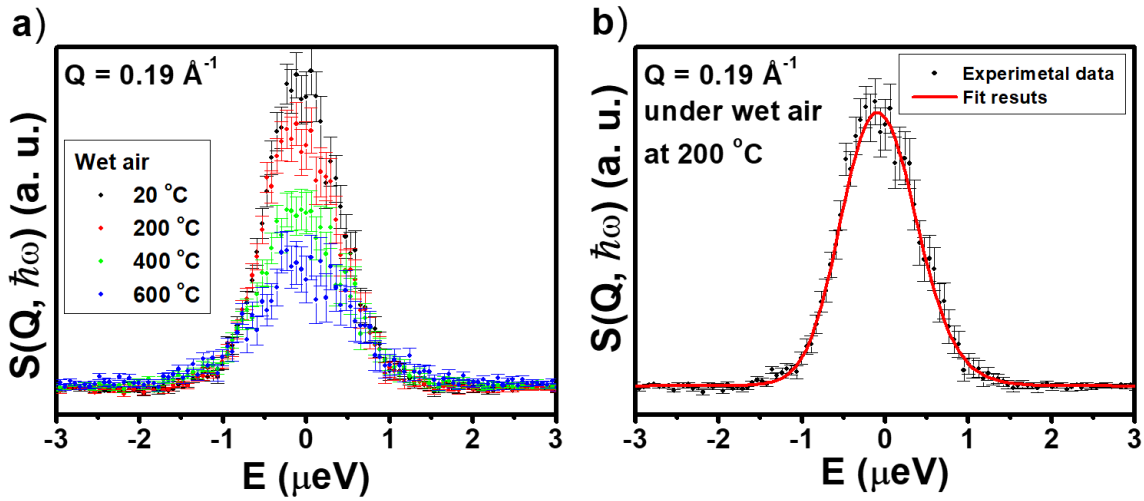

Figure 2. a) Neutron scattering spectra, $S(Q,\hbar\omega)$ of BCZY. Inset compares temperature effect on quasielastic dispersion. b) An example of QENS spectrum fitted using CEM. All spectra were collected between ±30 μeV, Figures present zoomed region.

Table 1. QENS parameters by CEM, where f corresponds to the fraction of fixed atoms and the mean residence time. Reduced chi-square parameter χ_r^2 (or commonly χ^2) indicates the goodness of fit.

T (°C)	f	l (Å)	τ (ps)	D_H (cm²/s)	χ^2
25	-	-	-		~0.7
100	-	-	-		~0.7
200	$0.8^{+0.1}_{-0.2}$	3.4 ± 0.2	400^{+1100}_{-215}		~0.9
300	0.6 ± 0.1	3.4 ± 0.1	290 ± 100	$6.6\pm2\times10^{-7}$	1.1
400	0.4 ± 0.1	3.4 ± 0.1	175 ± 30	$1.1\pm0.3\times10^{-6}$	1.3
500	0.4 ± 0.1	3.4 ± 0.1	130 ± 15	$1.5\pm0.3\times10^{-6}$	1.2
600	0.5 ± 0.2	3.4 ± 0.1	60 ± 5	$3.2\pm0.5\times10^{-6}$	1.0
700	-	-	-		0.8
800	-	-	-		0.7

Some comments from fits are described:

- At 25 and 100 °C, it is impossible to obtain any reliable parameters. For example, at 25 °C fixing f = 1 (no quasielastic) the fit gives $\chi^2 = 0.75$, while fixing f = 0 (only quasielastic term) one gets $\chi^2 = 0.69$ (with $l = 3.35$ Å and $\tau = 21000$ ps). In the same way, at 100 °C f = 1 gives $\chi^2 = 0.89$ and f = 0, $\chi^2 = 0.76$ (with $l = 3.30$ Å and $\tau = 13000$ ps). The reason is that the quasielastic contribution is so small that ignoring the Lorentzian contribution does not make a large difference on χ^2. On the other hand, setting f = 0 drives the fit to a very narrow Lorentzian that basically substitute the delta function.
- A similar behavior is observed at 200 °C. However, the quasielastic signal is large enough to restrict the possible range of valid parameters. For example, f = 1 gets $\chi^2 = 1.51$. And using f = 0, the $\chi^2 = 1.14$ and the fitted curve is clearly unable of reproducing well the intensity of the central peak. There is a strong correlation between the fraction of fixed atoms and the mean residence time, so there is a large set of possible pairs of (f, τ) values that fit the data with similar accuracy. Thus jump lengths are consistently found in the range 3.26 - 3.49 Å, but f can take values in the range of 0.6 and 0.9, while τ takes values in the range 1500 (for f = 0.6) and 185 (for f = 0.9) ps, all of them giving similar values of the reduced $\chi^2 < 1$.
- At 700 and 800 °C, the signal is so low and the relative error bars so large, that even fitting just with a flat background gives $\chi^2 = 0.96$ (at 700 °C) and 0.83 (at 800 °C), it is impossible to get any parameter with a reasonable accuracy.