Experimental report

09/02/2021

Proposal: 5-25-269 **Council:** 10/2018

Title: In-situ neutron diffraction study of BaCe0.4Zr0.4Y0.2O3-d proton conducting perovskite

Research area: Materials

This proposal is a resubmission of 5-25-268

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

Instrument	Requested days	Allocated days	From	To
D2B	3	3	11/10/2019	14/10/2019
D20	2	2	10/10/2019 13/01/2020	11/10/2019 14/01/2020

Abstract:

BaZrO3 and BaCeO3-based materials have potential application as electrolytes for solid oxide fuel cells (SOFCs) and electrolizer (SOECs) due to lower operating temperatures and higher efficencies with respect to commercial electrolytes. 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, for the BaCe0.4Zr0.4Y0.2O3-d perovskite we propose:
-to study phase transition from rhombohedral to cubic symmetry between 400 and 600 °C. This phase transition, associated to sample dehydration, was not observed by XRD techniques.
-to determine the structural features, particularly deuterium positions and occupations in the lattice, as well as oxygen related parameters, by obtaining high quality NPD patterns of wet (deuterated) and dry sample at 4 and 298 K under He atmosphere using a cryostat and vanadium sample holder and under wet (D2O vapor) and dry atmospheres between 298 and 1073 K.

Comments: This is resubmission of proposal 5-25-268, the requested instruments were very heavily overloaded during this round.

BCZY perovskite was synthesized by a solid state reaction (SSR) and sintered at 1600 °C for 12 hours [1,2]. Previously, the powders were annealed *in situ* at 800 ºC under dry synthetic air for 30 minutes, then at 400 ºC under wet (~ 2 % D_2O vapor) synthetic air for 2 hours inside the furnaces of ILL's neutron diffractometers. These thermal treatments ensure on a first step to lose all H_2O and then incorporate D_2O into the structure. The dynamic measurements were performed at D20 instrument by using wavelength (λ) of 1.544 Å using heating rates of 2 ºC/min on wet/dry samples. The heavy water vapor incorporation into a dry sample was followed at 400 ºC and hydration kinetics was estimated. The stationary measurements were performed at high resolution diffractometer D2B with λ = 1.594 Å and high flux mode, with a step of 100 ºC, under wet and dry synthetic air. The dwell time for each stationary measurement was at least 30 min. In both cases, the measurements were performed between 100 and 800 ºC, the λ were calibrated using diffraction standards, the patterns were collected in angular range (2θ) between 0.5 and 160 º and plotted in transference moment ($Q = (4\pi/\lambda) \sin \theta$). For heat treated measurements, the powders were placed in a quartz sample holder inside an induction furnace with a thin vanadium foil heater. The dynamic ND measurements allow to detect the temperature (T) of the 2nd order phase transition, i.e. rhombohedral $R\bar{3}c$ to cubic $Pm\bar{3}m$. In this sense, the stationary ND patterns were fitted by the Rietveld method using the Fullprof Suite [3] with a rhombohedral and cubic structural models [2,4]. The background, peak profile, crystallite size, Debye-Waller factors, etc., were fitted according to our previous work [2]. The oxygen and deuterium atomic positions and anisotropic atomic displacement parameters were refined and related to the structural distortion.

BCZY presents a protonic transport mechanism below 400 ºC, mixed conductivity by protons and oxygen vacancies between 400 and 600 ºC and oxygen vacancy conductivity above 600 ºC. In addition, this perovskite shows rhombohedral symmetry below 400 ºC and cubic from 600 ºC where the oxygen content (3-δ) was ≈ 2.9 (i.e. occupancy ~ 0.97) and maintained constant in whole T range according to the Y^{+3} doping [1][2]. In the same way, Malavasi *et al.* indicated that $BaCe_{0.85-x}Zr_xY_{0.15}O_{3-\delta}$ with x = 0.3 and 0.4 exhibited the same phase transition above 520 °C [4]. In addition, Mather *et al.* reported the Wyckoff positions (WP) of deuterium atoms into $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$ perovskite and 2nd order phase transition [5]. Figure 1a shows the collection of ND patterns of BCZY powder sample in the dynamic mode. The phase transition from rhombohedral to cubic symmetry was detected around 520 ºC. Also, a slope change at 4.75 $Å^{-1}$ was observed below the 2nd order phase transition (see Figure 1b). This cell shrinkage is in agreement with our previous studies [1,2].

Figure 2a compares ND patterns of wet and dry BCZY powders at 100 ºC, where the intensity (I) of some reflections is sensitive to D incorporation into the structure as interstitial sites $OD_O^{\bullet}$,according to the following reaction: $V_O^{\bullet\bullet} + D_2O_{(g)} + O_O^x \rightleftharpoons 2OD_O^{\bullet}$. The hydration reaction of oxygen vacancies $V_O^{\bullet\bullet}$ includes the oxygen sites O_O^x. During refinements of the BCZY dry powder sample, the oxygen content was fixed (i.e., 3-δ = 2.90, being the oxygen occupancy 0.9667) in the whole T range, while the wet powder requires some considerations:

(i) the D Wyckoff positions were assumed to be 36*f* and 12*h* for $R\bar{3}c$ and $Pm\bar{3}m$, respect. [5].

(ii) the O occupancy was full (i.e. 1) and D was considered 0.0334 according to defect reaction for T < 400 ºC [2].

(ii) the O and D content was calculated between 400 and 600 ºC. According to thermogravimetric (TG) and electrochemical (EIS) measurements, BCZY presents full hydration below 400 ºC, and fast dehydration above 500 ºC.

(iv) the O occupancy is 0.9667 for T > 700 ºC.

Figure 2b presents the refinement of ND patterns of wet BCZY powder sample at 100 °C. The heavy atoms (Ba and Ce/Zr/Y) were fitted with isotropic displacement parameters U_{iso}, meanwhile light atoms (O and D) were adjusted by anisotropic displacement parameters U_{aniso}. The equivalent U_{iso} for O and D were also considered (see Table 1). Figure 3 compares crystallographic parameters obtained from fits where BCZY suffers shrinkage between 500 and 600 ºC which is associated to the phase transition.

TG and EIS indicate that structural H_2O/D_2O loss occurs continuously between 400 and 600 ºC. Therefore, the 2nd order phase transition and structural water loss are separate processes and the phase transition does not affect the protonic conductivity transport mechanism.

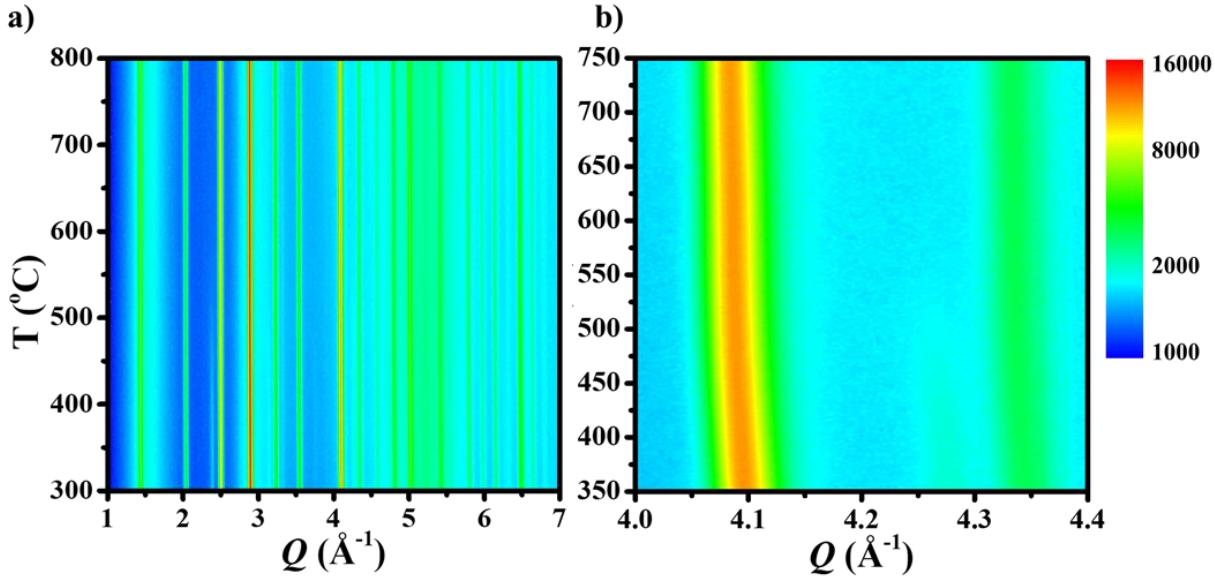

Figure 1. a) Evolution of the ND patterns with T while heating a wet sample. b) The selected zone reveals a slope change which is associated with the phase transition. In both cases, intensity levels are presented in a logarithmic scale.

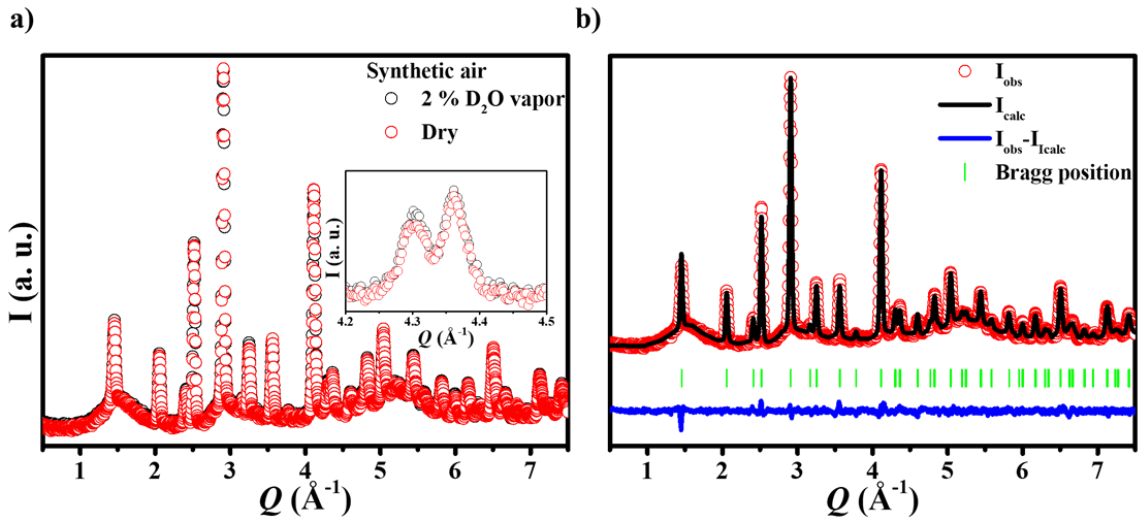

Figure 2. a) ND patterns collected under dry and wet synthetic air at 100 ºC. The inset indicates a reflection sensitive to D_2O vapor incorporation. b) Refinement of BCZY wet powder samples. The intensities are expressed in arbitrary units (a. u.).

Table 1. Crystallographic parameters from refinement of BCZY wet powder sample at 100 ºC under wet (~ 2 D_2O % vapor) synthetic air.

$R\bar{3}c$ (Nº 167) Space group **$a = b = 6.1145(3)$ Å, $c = 14.9393(8)$ Å, $\alpha = \beta = 90$ º, $\gamma = 120$ º, $V = 483.71(4)$ Å^3** **$R_p = 17.4$ % , $R_{wp} = 10.7$ %, $\chi^2 = 2.70$**								
Atom	**WP**	**Occ.**	**Atomic position**			**Displacement parameters (×10^2) (Å^2)**		
						Anisotropic		**Isotropic**
			x	**y**	**z**	**$U_{11} = U_{22}$**	**U_{33}**	**U_{iso}**
Ba	**6*a***	**1**	**0**	**0**	**0.25**			**2.75(6)**
Ce	**6*b***	**0.4**	**0**	**0**	**0**			**1.29(4)**
Zr		**0.4**						
Y		**0.2**						
O	**18*e***	**1**	**0.464(1)**	**0**	**0.25**	**5.61(5)**	**1.62(4)**	**4.28(4)**
D	**36*f***	**0.0334**	**0.146(7)**	**0.493(9)**	**0.035(3)**	**7.32(4)**	**2.45(7)**	**7.32(5)**

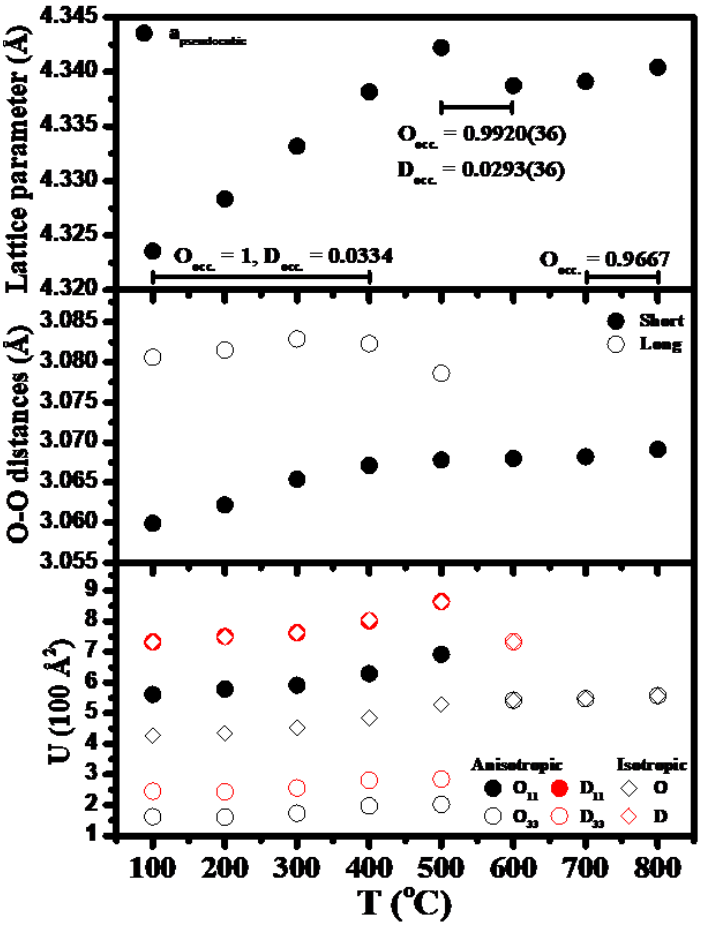

Figure 3. Pseudocubic lattice parameters, oxygen distances and Debye-Waller factors as a function of T under wet synthetic air. The occupancies of O and D considered during ND refinement at each temperature are indicated in the first plot.

References

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