Experimental report

08/01/2024

Proposal: 5-21-1180 **Council:** 4/2023

Title: Structure of BaZrxCe0.8-xY0.1Yb0.1O3-delta (0 <= x <= 0.8) proton conductors at room temperature and fuel cell operating temperature.

Research area: Materials

This proposal is a new proposal

Main proposer: Eric QUAREZ

Experimental team: Lozane HAMZE
Eric QUAREZ

Local contacts: Emmanuelle SUARD

Samples: BaZrxCe0.8-xY0.1Yb0.1O2.9 (0 <= x <= 0.8)

Instrument	Requested days	Allocated days	From	To
D2B	3	3	24/11/2023	27/11/2023

Abstract:

Proton conductors based on Ba(Zr,Ce)O3-delta perovskites have been proposed as electrolytes and electrodes for proton-conducting solid oxide cells (PC-SOCs), i.e., fuel cells (PC-SOFCs) and electrolysers (PC-SOECs). Co-doping of barium zirconate-cerate with Y and Yb has been shown to improve ionic conductivity, catalytic activity for hydrocarbon reforming and stability for high Zr content. The structure of Yb-based compounds (called BZCYYb) has not been carefully studied in the literature. This proposal aims to fill this gap by studying the structure of five BZCYYb compositions (three intermediate and two terminal compositions) at room temperature and fuel cell operating temperature. Neutron diffraction is the only diffraction technique capable of detecting slight distortion of the oxygen lattice and providing the effective structure.

The Ba(Zr,Ce,Y)-based oxide materials are widely studied as proton-conducting electrolytes in solid oxide fuel cells [1]. The experiment using D2B instrument at ILL (24-27 November 2023) enabled us to record data at room temperature for four $BaZr_xCe_{0.8-x}Y_{0.1}Yb_{0.1}O_{2.9}$ compositions (x = 0.0, 0.1, 0.2, 0.3), as well as temperature-dependent data up to 700°C for compositions x = 0.1 and x = 0.3. The aim of the experiments is to build a phase diagram of the $BaZr_xCe_{0.8-x}Y_{0.1}Yb_{0.1}O_{2.9}$ solid solution between x = 0.0 and x = 0.8. This study can be related to the study by Malavasi in which the authors built a phase diagram of the $BaCe_{0.85-x}Zr_xY_{0.15}O_{3-\delta}$ solid solution between x = 0.1 and x = 0.4 [2]. The Yb introduced into current materials is expected to increase stability and conductivity levels [3-4]. Initial results show that the phase diagram obtained for Yb-containing materials is significantly different from that for Yb-free materials. The symmetry adopted by the Yb-based phases and the type of transition are remarkably distinct.

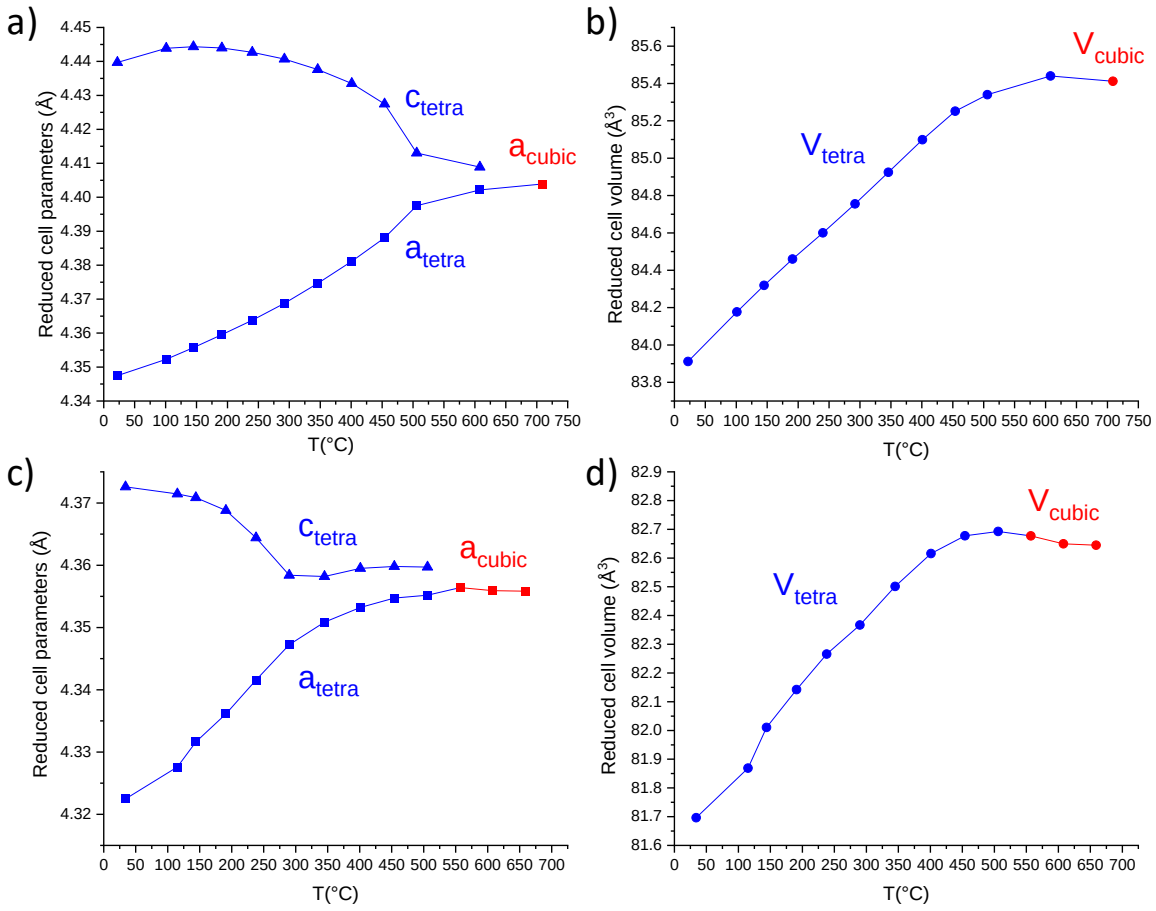

Figure 1. Reduced cell parameters and reduced cell volume of $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{2.9}$ (a,b) and $BaZr_{0.3}Ce_{0.5}Y_{0.1}Yb_{0.1}O_{2.9}$ (c,d) samples obtained by Rietveld refinement of neutron powder diffraction data collected at D2B as a function of temperature.

Figure 1 shows the evolution of the cell parameters and cell volume of the $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{2.9}$ (a,b) and $BaZr_{0.3}Ce_{0.5}Y_{0.1}Yb_{0.1}O_{2.9}$ (c,d) samples as a function of temperature, based on neutron powder diffraction data collected at D2B instrument. The compounds show a phase transition from tetragonal to cubic symmetry at decreasing temperature as x increases. Compound x = 0.2 adopts tetragonal symmetry at room temperature, as expected. For compound x = 0.0, the structure may exhibit less than tetragonal symmetry at room temperature, as the structure in tetragonal symmetry does not give satisfactory agreement factors. The work is still in progress. We also noticed, for temperature dependent experiments, that after the phase transition, the cubic volume does not increase with temperature as expected, but decreases slightly.

Figure 2a shows the final Rietveld refinement plot for the $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{2.9}$ sample. The agreement factors are all acceptable and all atomic displacement parameters were anisotropically refined (Figure 2b) confirming the choice of structural model and the quality of the data. A publication dealing with the structure of the x = 0.1 sample is in progress, using a combination of X-Ray and neutron Rietveld refinements.

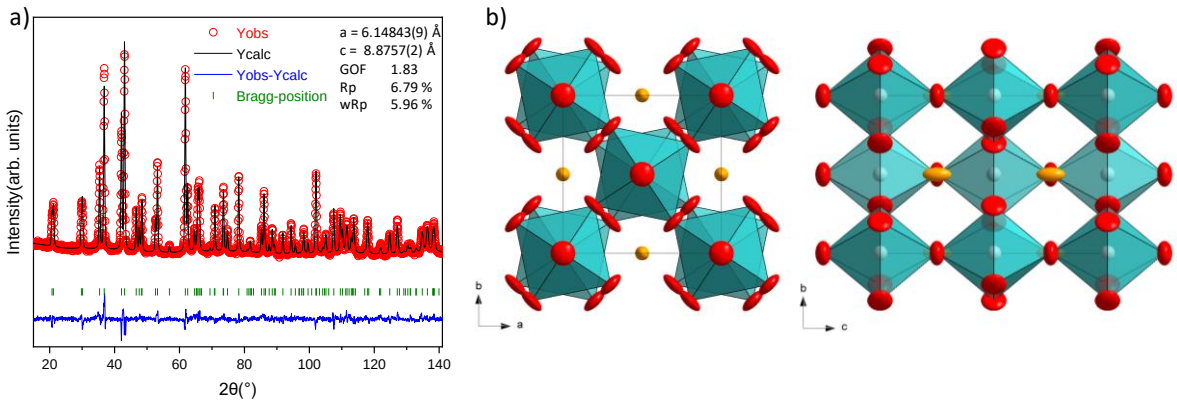

Figure 2. (a) Rietveld refinement of the neutron powder diffraction data of $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{2.9}$ sample collected at room temperature at D2B and (b) corresponding crystallographic representations.

To finalize the phase diagram of the $BaCe_{0.85-x}Zr_xY_{0.15}O_{3-\delta}$ solid solution, neutron data from samples x = 0.0 and x = 0.4 are required, which is the subject of a new proposal.

References

[1] Adv. Energy Mater. (2023) 2302175
[2] Chem. Mater. 23 (2011) 1323
[3] Science 326 (2009) 126
[4] Nature Energy 3 (2018) 202