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Insight into the dehydration behaviour of scandium-substituted barium titanate perovskites *via* simultaneous *in situ* neutron powder thermodiffractometry and thermogravimetric analysis

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ABSTRACT

Hydration-dehydration cycles are critical to the mechanical performance of ceramic proton conductors. The development of *in situ* methods is desirable in order to study their structural response under conditions that mimic the operating ones. Neutron powder diffraction studies combined with simultaneous thermogravimetric analysis were performed on the hydrated forms of two members of the oxygen deficient perovskite $BaTi_{1-x}Sc_xO_{3-\delta}$ series, with $x = 0.5$ and $x = 0.7$. Rietveld analyses agreed with *in situ* gravimetric data, allowing correlation of occupancy factors of the oxygen site to hydration levels and other structural data. Dehydration is an activated process that impacts on structural parameters and the level of Sc substitution was found to control the structural response during *in situ* dehydration, with higher Sc content leading to significantly greater volume contraction. This was rationalised by the chemical expansion due to hydration of oxygen vacancies within the $x = 0.5$ sample being anomalously small. Furthermore, the behaviour of the $x = 0.5$ system revealed an unexpected cell expansion during the early stages of dehydration, suggesting the hydration level may influence the thermal expansion coefficient (TEC).

1. Introduction

The success of proton conducting-solid oxide fuel cells (PC-SOFC, or PCFC) technology relies on understanding the transport properties and probing the stability of the materials utilised to fabricate the cell. To this end, the toolkit available to the materials scientist is ever increasing, with a number of characterisation methods contributing to elucidating structure-property relationships [1]. Often, independent or *ex situ* studies fail to comprehensively explain processes, due to difficulties to exactly reproduce conditions. Hence, the development of *in situ*, *in operando* and combined method approaches is very desirable [2], and demonstrated, for example, by studies on hydrogen storage materials [3], Li-ion batteries [4], oxide systems for carbon sequestration [5], catalytic systems [6], and protonic conductors [7, 8].

High temperature proton conducting electrolytes are the benchmark among acceptor doped perovskite-type materials, with the $BaCeO_3$ and $BaZrO_3$ related phases considered as the most promising [1]; among those, Y-doped $BaZrO_3$ [9] proton conductors display the highest bulk proton conductivity [10, 11]. Commercialisation of this class of ceramic materials remains an ongoing endeavour, mainly because of the high grain boundary resistance due to a bimodal size distribution of grains [12, 13] that affects their sinterability and stability under operating conditions. Optimisation of the parameters governing densification and stability of such phases is being addressed by novel fabrication methods [14–16] and grain surface processing prior to utilisation [17].

In order to conduct protons, these oxides undergo a hydration step, illustrated in the Kröger-Vink notation by the equilibrium:

$$H_2O\,(g) + v_O^{\bullet\bullet} + O_O^{\times} \rightleftarrows 2\,OH_o^{\bullet} \tag{1}$$

where water from the gas phase is incorporated into the vacancies generated by acceptor doping the host phase, *i.e.* the original mixed oxide itself, thus creating protonic defects within the lattice in the form of hydroxyl anions at an oxygen lattice site. Hydration is usually associated with an expansion of the crystal lattice [18, 19], a phenomenon that is critical to the mechanical stability and, therefore, to the lifetime of any device, potentially leading to micro-fissures in the

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electrolyte and/or delamination at the electrolyte/electrode interface. Further, filling the vacancies in systems with high levels of oxygen vacancies can produce structural phase transitions, as in the case of the orthorhombic to tetragonal transition that accompanies the transformation of the brownmillerite phase $Ba_2In_2O_5$ to $Ba_2In_2O_5(H_2O)$ [20]. Likewise, in Y-doped $BaCe_{1-x}Y_xO_{3-\delta}$, a more relevant system for PCFC applications, neutron diffraction experiments performed on the $x = 0.20$ solid solution show transitions at 773 K (orthorhombic, *Imma*), 873 K (rhombohedral, $R\bar{3}c$), and 1073 K (cubic, $Pm\bar{3}m$) [21] and the stability of the phases can be correlated with the degree of hydration. Phase transitions are suppressed by the presence of oxygen vacancies and the protonic defects increase the tendency for octahedral tilting, as shown by Andersson et al. [8]. This shifts the stability of lower symmetry phases to higher temperatures and promotes a monoclinic $I2/m$ structure at temperature below 673 K. These examples show that the hydration-dehydration behaviour in proton conductors can be complex. Development of methods to investigate systems under conditions that mimic those found in a device is necessary and may also shorten the development cycle of new materials.

Relatively few studies have focussed on the proton conductivity of $BaTiO_3$-based solid solutions, and most concern pristine or 5–10% doped materials [11, 22–26]. The main investigations on heavily doped titanate phases are ionic conduction studies of doped brownmillerite $Ba_2In_2O_5$ [27, 28]. Here, progressively replacing Ti for In induces disordering of the vacancy array, stabilising cubic perovskite structures at room temperature for substitutions larger than 15%. $BaIn_{0.8}Ti_{0.2}O_{3-\delta}$ displays the highest proton conductivity ($1.1 \times 10^{-3}\ S\,cm^{-1}$, under wet N_2 at 723 K), but also a phase transition from cubic $Pm\bar{3}m$ to tetragonal $P4/mmm$ upon hydration [29]. Higher doping levels ($\geq$50%) fully stabilise cubic structures, but show poorer protonic conduction [30]. This may be linked to the irregular oxygen sublattice built up by a combination of regular InO_6 and distorted TiO_6 octahedra [31]. A more regular framework for proton mobility is obtained by replacing In^{3+} with the smaller Sc^{3+} (0.80 Å *vs.* 0.74 Å, respectively, when 6-coordinated) that has a strong preference for octahedral environments. The 50% Sc-substituted $BaTiO_3$ [32] is a better proton conductor than its In-doped counterpart [30], under similar conditions. Its proton transference number, t_{H^+}, is close to unitary, below 773 K in a wet inert atmosphere. The 70% Sc-substituted material is able to maintain the same t_{H^+} at higher temperatures [33]. Interestingly, in the $BaTi_{1-x}Sc_xO_{3-\delta}$ system, the Sc doping is structure directing. X-ray diffraction data [33] revealed a phase transformation from a 6H hexagonal perovskite structure for compositions $0.1 \leq x \leq 0.2$, to a cubic perovskite for $0.5 \leq x \leq 0.8$, with an intermediate multiphasic region when $0.3 \leq x \leq 0.5$. In the same study, impedance spectroscopy analyses show how the structural transition impacts on proton mobility, with the highest proton conductivity measured for the cubic $x = 0.7$ (*ca.* $2 \times 10^{-3}\ S\,cm^{-1}$), whereas in the hexagonal $x = 0.2$ sample performance is reduced by two orders of magnitude, under the same conditions [33]. The behaviour was investigated [34] by means of neutron powder diffraction (NPD) and thermogravimetric analysis (TG), coupled with predictions based on first principle calculations. Ordering of metal dopant, oxygen vacancies and protonic defects was found in the hexagonal $x = 0.2$ type, where protons diffuse *via* higher energy positions. On the contrary, the cubic $x = 0.7$ type is characterised by disorder.

It is clear that Sc levels have a profound effect on the physical properties of these titanate phases and that the cubic members are more interesting from the point of view of the technical applications. Further, a striking point about the 50% Sc-substituted material is that it displays very little chemical expansion of its lattice with the filling of vacancies [32], as per hydration reaction (1). Given the large amount of vacancies that the material can host and that can be filled with protonic defects, this reveals a property that can be crucial for its application as a proton conducting membrane in commercial devices.

This work, hence, explores hydration levels and structural response with a simultaneous thermogravimetric (TG) and *in situ* neutron powder diffraction (NPD) study on two cubic members of the $BaTi_{1-x}Sc_xO_{3-\delta}$ series, with $x = 0.5$ and $x = 0.7$ (BTS50 and BTS70, respectively). With neutrons, crystallographic sites bearing lighter atoms, such as oxygen, can be investigated even in the presence of heavier elements. Therefore, following the evolution of the oxygen site occupancy during dehydration becomes possible, in order to directly link structural parameters and hydration levels to observed mass losses. The structural evolution due to dehydration is discussed in terms of the combination of thermal and chemical expansion in the two systems, and the relative size of vacancies and protonic defects. The aspect of method development is equally important as we hope that demonstrating the feasibility of the experiment will allow further studies on proton conductors and other related materials.

2. Experimental

BTS50 and BTS70 were prepared by solid-state reaction, using carbonate and oxides: $BaCO_3$ (Alfa Aesar, 99.8%), TiO_2 (Sigma-Aldrich, 99.8%), Sc_2O_3 (Alfa Aesar, 99.9%). TiO_2 and Sc_2O_3 were annealed at 1273 K overnight, then stored in a drying oven at 423 K, along with $BaCO_3$, prior to mixing. Stoichiometric mixtures were prepared by manually grinding the reactants in an agate mortar, with ethanol as suspending agent to enhance homogenisation. The finely mixed powders were fired at 1273 K in α-alumina crucibles, then intensively ground and pelletised. The same operations were repeated for every following heating step until phase purity was satisfactory. BTS50 was annealed up to 1773 K, and BTS70 up to 1798 K, with intermediate grinding and pelletising. During the synthesis, sacrificial loose powder was used to cover the faces of the pellets in order to limit volatilisation of BaO, and Ti ions diffusion into the alumina crucible. The samples, placed into α-Al_2O_3 boats, then underwent a hydration step, carried out in a tube furnace through which nitrogen (Air Liquide Alphagaz 1, containing 6 ppm of H_2O) was passed, after bubbling through a round bottom flask filled with distilled water maintained at a constant temperature of 333 K, providing a $p(H_2O)$ of *ca.* 0.2 atm. The samples were exposed to a stepwise temperature programme, from 1073 K to 423 K using the method described in a previous study [34].

Laboratory X-ray powder diffraction data were collected using a Bruker AXS D8 Advance diffractometer equipped with a copper target, a Ge (111) primary monochromator (providing Cu $K\alpha_1$ radiation with $\lambda = 1.54056$ Å), and a solid state LynxEye detector. Data were analysed by means of the Rietveld method [35], using the academic version of the software TOPAS v5 [36] (Bruker AXS). The background was modelled with a Chebyshev polynomial function and peak shapes by a convolution of two back-to-back exponentials with a pseudo-Voigt function. For the RT datasets, structural parameters, occupancy factors for the Sc/Ti site, and isotropic displacement parameters were refined. Sequential refinements were performed on cubic lattice parameters, all atomic displacement parameters (ADPs), oxygen site occupancy factors (SOFs), with constrains on Sc/Ti SOFs.

Ex situ thermogravimetric analyses (TGA) were performed on the hydrated samples, in order to determine the degree of saturation of the oxygen vacancies, according to (1). Measurements were carried out on samples of about 60 mg loaded in small α-alumina pans (6 mm diameter), using a Netzsch STA 409 PC Luxx. Temperature programmes were set from room temperature up to 1073 K, at heating rate of 15 K/min, under a flow of 20 ml/min of nitrogen (Air Liquide Alphagaz 1, containing 6 ppm of H_2O).

In situ high-resolution diffraction data were collected on the time-of-flight instrument Polaris at the ISIS neutron and muon source. The samples were loaded into open, cylindrical 8 mm external diameter vanadium cans, then hooked by a fine tungsten wire to the balance of the IGA^n (Intelligent Gravimetric Analyser for neutron experiments, Hiden Isochema) and enclosed in a quartz tube sealed by a Cu gasket. The sample environment was heated up to 573 K by two resistive coils,