



Study of the hydration level in proton conducting oxides using neutron diffraction with polarization analysis



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ABSTRACT

We report results from neutron diffraction with polarization analysis of the effect of In dopant level on the hydrogen concentration in hydrated samples of the proton conducting perovskite type oxide $\text{BaZr}_{1-x}\text{In}_x\text{O}_{3-x/2}$ with $x = 0, 0.175, 0.20, 0.225, 0.25,$ and 0.275 . Analysis of the neutron data establishes a trend of increasing hydrogen concentration, which is comparable to that obtained from thermogravimetric measurements on the same samples, as well as an increased unit-cell size and local structural disorder as a function of increasing In dopant level. These results encourage further use of neutron diffraction with polarization analysis as a non-destructive technique for the determination of the total hydrogen concentration, and structural properties, of proton conducting oxides as well as other hydrogen-containing materials.

1. Introduction

Proton conducting perovskites are currently receiving considerable attention because of their promise as electrolytes in various electrochemical applications [1,2]. The protons are not native members of the host lattice but are introduced by a process involving acceptor-doping and hydration. The acceptor-doping, such as In substituted for Zr in BaZrO_3 , results in the formation of oxygen vacancies. Upon exposure of the material to humid atmospheres, hydroxyl groups ($-\text{OH}$) are incorporated onto the formerly vacant oxygen sites whereas the remaining protons bind to other oxygens of the perovskite lattice.

The concentration of hydrogen (protons), which is an important property affecting the proton transport characteristics in these materials, is routinely determined from thermogravimetric analysis (TGA) [3–5]. This laboratory technique is accurate and relatively fast, but it is destructive. Moreover, it detects only chemical species that are volatile in the temperature range of the measurements and relies on several assumptions regarding the chemical composition and the temperature behaviour of the studied material. A typical challenge with TGA and perovskites in particular is the possible weight loss due to CO_2 taking place at high temperatures if carbonates are present as residual impurities from the synthesis process. This undesired contribution can be distinguished by coupling TGA with mass spectroscopy [5]. In comparison, neutron techniques such as prompt-gamma activation analysis (PGAA) and neutron diffraction with polarization analysis (or polarized

neutron diffraction, pND) provide non-destructive methods to determine the total hydrogen concentration in samples with high sensitivity and accuracy. Furthermore, these techniques provide additional information: PGAA makes it possible to determine also the concentration of the other elements in proton conducting oxides with the exception of oxygen, whereas pND allows to obtain a diffraction pattern in which the contributions from nuclear (*i.e.* coherent and incoherent), spin incoherent and magnetic scattering can be separated and analyzed. Measurements can be performed quite straightforwardly, using the same sample cells as may have been used, or will be used, in other neutron scattering experiments, *e.g.* inelastic scattering experiments. Moreover, although limited by the currently available instrument resolution and accessible momentum transfer (Q) range [6], information regarding the modifications induced by the dopant on the structure may be inferred [7].

In previous neutron studies focusing on the determination of the concentration of atomic species in proton conducting oxides, PGAA has been used for hydrated samples of $\text{BaPr}_{1-x}\text{Y}_x\text{O}_{3-x/2}$ with $x = 0, 0.10, 0.15,$ and 0.20 , and for $\text{BaCe}_{0.90}\text{Y}_{0.10}\text{O}_{3-x/2}$ [8], whereas pND has been used for hydrated samples of $\text{BaZr}_{1-x}\text{M}_{0.1}\text{O}_{3-x/2}$ with $M = \text{Y}$ and Sc , and $\text{BaZr}_{1-x}\text{In}_x\text{O}_{3-x/2}$ with $x = 0.10, 0.20$ and 0.25 [7,9]. For the In doped samples, an increased unit cell and local as a function of increasing In doping concentration were found [7]. In the present work, we expand the In dopant modification by performing a systematic pND study of the hydrogen concentration in $\text{BaZr}_{1-x}\text{In}_x\text{O}_{3-x/2}$ with

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$x = 0.175, 0.20, 0.225, 0.25,$ and 0.275 . The aim of the study is to investigate the effect of the In dopant level on the total hydrogen concentration, to compare with the hydrogen concentration determined by TGA on the same sample specimens, and to discuss the key aspects of pND measurements on proton conducting oxides generally. Additionally, since the $\text{BaZr}_{1-x}\text{In}_x\text{O}_{3-x/2}$ system exhibits an average-cubic structure (space group $Pm\bar{3}m$) for the chosen compositions [10,11], the pND data gives useful structural information regarding both the unit-cell size and local structural disorder, as a function of In dopant level, with the average-cubic structure preserved.

2. Experimental

2.1. Sample preparation

Samples with the compositions $\text{BaZr}_{1-x}\text{In}_x\text{O}_{3-x/2}$ ($x = 0, 0.175, 0.20, 0.225, 0.25,$ and 0.275) were prepared by conventional solid state synthesis, following the procedure as described in Ref. [7]. The as-sintered samples were vacuum dried at 950°C for 12 h (at a pressure $< 10^{-5}$ mbar inside a sealed tube furnace), followed by hydration in a hydrothermal autoclave at 185°C for a period of 15–18 h. The hydrated samples are hereafter labelled as BZO (for $x = 0$), 17.5In:BZO (for $x = 0.175$), 20In:BZO (for $x = 0.20$), 22.5In:BZO (for $x = 0.225$), 25In:BZO (for $x = 0.25$), and 27.5In:BZO (for $x = 0.275$), respectively.

2.2. Polarized neutron diffraction

pND [6,12] was carried out at the cold neutron diffractometer D7 at the Institut Laue-Langevin (ILL) in Grenoble, France, on all samples. The used incident neutron wavelength was 4.8 \AA , giving access to a measurable Q range of $0.25\text{--}2.47\text{ \AA}^{-1}$. The powder samples were placed in cylindrical cells of aluminium (Al) with annular geometry (one may note that a cell of vanadium (V) could also be used, but is less preferable because it would contribute to the spin-incoherent background which lowers the sensitivity for hydrogen, see further below). The outer diameter of the sample cell was 20 mm, and the inner diameter was tuned between 8.5 and 13 mm by using different Al inserts in order to keep the total scattering of neutrons to 13–15% so that the intensity is optimized at the same time as the effect of multiple scattering is kept at a relatively low level.

In the xyz -polarization analysis, the spin-flip and non-spin-flip cross sections for three orthogonal orientations of the neutron beam polarization are measured and, from linear combinations of these, the nuclear, spin incoherent, and magnetic scattering differential cross sections ($d\sigma/d\Omega$) can be derived [6]. The measurement of a vanadium standard of known mass enables to obtain these quantities in absolute units. Measurements of cadmium and quartz standards were used for the correction for beam attenuation and flipping-ratio calibration, respectively. A measurement of an empty container was used for sample-holder subtraction. The measurements were performed at room temperature, $T \approx 300\text{ K}$.

The spin incoherent scattering cross section, $(d\sigma/d\Omega)_{\text{inc}}$, averaged in the Q range $0.5\text{--}1\text{ \AA}^{-1}$ was used to derive the hydrogen concentration in the materials. The contribution of the hydrogen is singled out by subtracting those of all the other atoms according to the following relationship:

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{inc}}^{\text{H}} = \left(\frac{d\sigma}{d\Omega}\right)_{\text{inc}} - \sum_{i \neq \text{H}} \frac{\sigma_{\text{inc}}^i n^i}{4\pi}. \quad (1)$$

Here $(d\sigma/d\Omega)_{\text{inc}}^{\text{H}}$ is the spin incoherent scattering cross section of hydrogen, and σ_{inc}^i refers to the spin incoherent scattering cross section of the i th element in the compound ($i = \text{Ba}, \text{Zr}, \text{In}, \text{O}$) weighted for its stoichiometric factor n^i . It should be noted that the contribution to the spin incoherent cross section from the other elements in the sample is very small in comparison with that of hydrogen [13]. Dividing $(d\sigma/d\Omega)_{\text{inc}}^{\text{H}}$ by $\sigma_{\text{inc}}^{\text{H}}/4\pi$ yields the hydrogen stoichiometric factor.

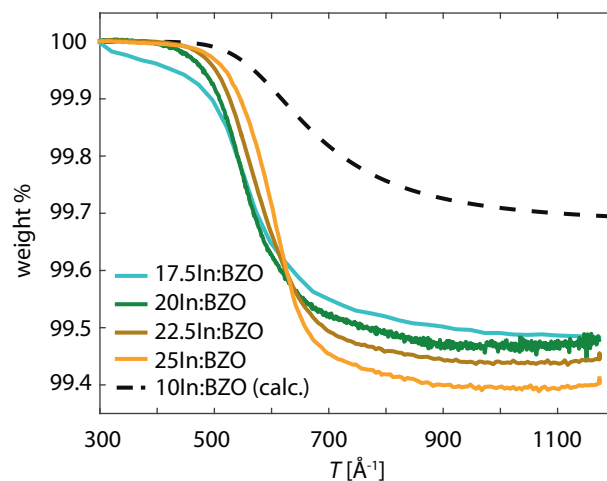


Fig. 1. Solid lines are dehydration curves obtained by TGA. The dashed line shows the theoretical dehydration curve for 10In:BZO in a dry-air atmosphere.

$d\Omega)_{\text{inc}}^{\text{H}}$ by $\sigma_{\text{inc}}^{\text{H}}/4\pi$ yields the hydrogen stoichiometric factor.

2.3. Thermogravimetric analysis

TGA was performed on the 17.5In:BZO, 20In:BZO, 22.5In:BZO and 25In:BZO samples using a TG 209 F1 Iris instrument from Netzsch. For each measurement, about 100 mg of sample was placed in an open platinum pan and heated from 300 to 1200 K with a heating rate of 5 K/min, under a flow of N_2 gas (25 ml/min).

3. Results and discussion

3.1. Thermogravimetric analysis

Fig. 1 shows the TGA curves for 17.5In:BZO, 20In:BZO, 22.5In:BZO and 25In:BZO, together with the theoretical curve for 10In:BZO as derived from the theoretical concentration of protonic defects $[\text{OH}^{\cdot}]$ calculated from the equation [14]

$$[\text{OH}^{\cdot}] = 3 \frac{p_w K}{p_w K - 4} \left[1 - \sqrt{1 - \frac{p_w K - 4}{p_w K} \left(\frac{2[\text{In}]}{3} - \frac{[\text{In}]^2}{9} \right)} \right]. \quad (2)$$

Here p_w is the vapour partial pressure, as set to 0.0126 bar in order to approximate a dry-air condition, K is the equilibrium constant for the dehydration process, and $[\text{In}]$ is the In concentration. The temperature dependence of K was calculated using hydration standard-state enthalpy and entropy values from Ref. [3].

A general trend observed in Fig. 1 is the increasing weight loss as a function of increasing In dopant concentration, as expected based on the filling of oxygen vacancies created by the In doping. For the material with the lowest In concentration, 17.5In:BZO, the gradual dehydration with increasing temperature starts already just above room temperature, whereas for the materials with higher In concentration, 20In:BZO, 22.5In:BZO and 25In:BZO, the initial dehydration starts at a higher temperature, $T \approx 500\text{ K}$. The significant weight loss for 17.5In:BZO in the low-temperature regime below 500 K is not expected for any In doped BaZrO_3 material on the basis of thermodynamic parameters, as exemplified by the theoretical curve in Fig. 1. A comparison with the literature of TGA data on proton conducting oxides suggests that the initial weight loss for 17.5In:BZO is related to the loss of physisorbed water molecules [15]. Assuming the contribution of bulk protons is dominant at $T > 500\text{ K}$, the level of dissolved protons seems increasing with increasing In concentration, as expected.

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