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Yttrium and hydrogen superstructure and correlation of lattice expansion and proton conductivity in the $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ proton conductor

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Bragg reflections in Y-resonant x-ray diffractograms of $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ (BZY10) reveal that Y is organized in a superstructure. Comparison with neutron diffraction superstructure reflections in protonated/deuterated BZY10 suggests that both superstructures are linked, and that protons move in the landscape imposed by the Y. The thermal lattice expansion decreases abruptly for protonated BZY10 at $T \geq 648 \pm 20$ K, coinciding with the onset of lateral proton diffusion and suggesting a correlation of structural changes and proton conductivity. The chemical shift in the Y L_1 -shell x-ray absorption spectra reveals a reduction from Y^{3+} toward Y^{2+} upon protonation. © 2009 American Institute of Physics. [doi:10.1063/1.3268454]

Many perovskite-type ceramics exhibit proton conductivity¹ and receive attention because of their potential applications as gas sensors, batteries, and electrolytes in intermediate temperature fuel cells and electrolyzers. We study here the example $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ (BZY10), which, like its parent compound BaZrO_3 , is an ABO_3 -type perovskite with the B-atom in an octahedral oxygen environment, as illustrated in Fig. 1(a).¹ Partial substitution of the Zr^{4+} by Y, which tends to have Y^{3+} valence, then generates an oxygen vacancy V_{O} , a double positively charged point defect [Fig. 1(b)]. Understanding the structure-property relationship of proton conductors on the molecular scale is essential for improving them for applications. While basic understanding of proton conductivity in ceramics is still lacking, it is believed that V_{O} assists in the dissociation of adsorbed water molecules (hydration) under ambient conditions according to the reaction^{2,3} $\text{H}_2\text{O}(\text{g}) + V_{\text{O}} + \text{O}_{\text{O}}^x \leftrightarrow 2(\text{OH}_{\text{O}}^+)$, then forming two pseudohydroxyl groups (OH_{O}^+), both of which denote a proton bound to a lattice oxygen O_{O}^x [Fig. 1(c)]. Proton diffusion is believed to be a two-step process [Fig. 1(d)], where at moderate temperatures T protons reorient with high frequency locally around a lattice oxygen ion with activation energy E_a in the order of few millielectron volt.⁴ At higher T the proton may overcome the activation barrier, which is in the order of 0.1 to 1.0 eV, leaving this site and jumping to another oxygen.⁵ Views are controversial on how structure parameters relate to proton transport. On the one hand it was found that E_a decreased with increasing oxygen ion distance,⁶ but molecular dynamics predicted that the energetic barrier is drastically lowered by shortening of the oxygen separation.⁷ Recent findings in our laboratory suggest that E_a increases with decreasing lattice spacing.⁸ Quantum molecular dynamics studies on yttrium substituted barium

zirconate show that protons have little interaction with their next neighbor oxygen ions, indicating weak hydrogen bond formation.⁹ Based on neutron diffraction data, potential proton positions in proton conductors have been suggested, but it is still unknown where exactly in the lattice the proton is accommodated.¹⁰

We synthesized three batches of $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ using a solid-state method,¹¹ one heated to 1173 K and cooled in dry N_2 and the other two heated in $\text{H}_2\text{O}/\text{N}_2$ and $\text{D}_2\text{O}/\text{N}_2$, respectively, at 723 K for 24 h. The latter two treatments were performed to achieve hydrogen and deuterium incorporation. The $\text{H}_2\text{O}/\text{N}_2$ and $\text{D}_2\text{O}/\text{N}_2$ atmospheres were obtained by bubbling N_2 through H_2O and D_2O , respectively. Neutron powder diffractograms (NPD) for the three samples were recorded from 300 to 773 K in steps of around 100 K with $\lambda = 1.1545$ Å (HRPT diffractometer,¹² SINQ Neutron Spallation Source). Anomalous x-ray diffraction data on the dry sample for the yttrium K -edge were collected at the Swiss Light Source,¹³ at 16, 16.9, 17, and 18 keV photon energy from 300 to 773 K in steps of around 100 K. Y L_1 -edge x-ray absorption spectra were collected at Beamline 9.3.1, Ad-

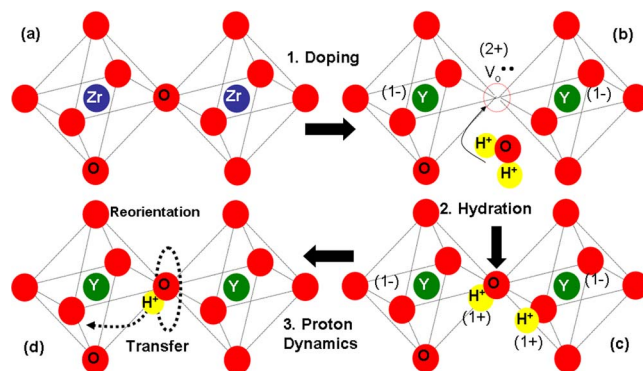


FIG. 1. (Color online) Schematic of Y substitution (acceptor doping), hydration (proton loading), and proton dynamics in BZY10 [(reproduced after (Ref. 1)].

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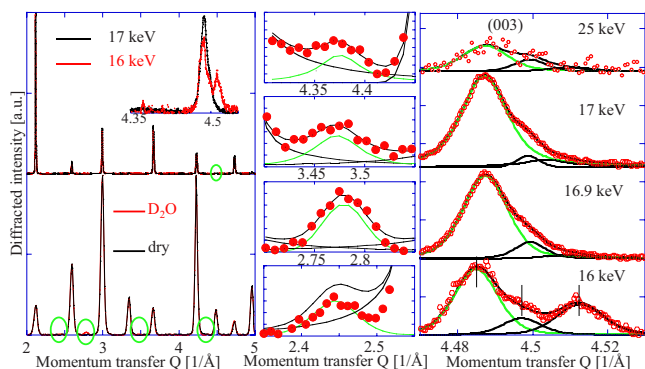


FIG. 2. (Color online) Synchrotron x-ray diffractograms recorded at 16 and 17 keV of dry BZY10 (upper left panel) and neutron diffractograms (ND) of deuterated and dry BZY10 (lower left). Green circles in the ND denote extra reflections from deuteration, magnified in the middle panel. Green circle in upper left panel denotes the (300) reflection, as magnified therein for 16 and 17 keV. Right panel shows evolution of (300) intensity and shoulders as a function of photon energy.

vanced Light Source, Berkeley, CA from 2370–2400 eV in steps of 0.1 eV and a resolution of $\Delta E/E \sim 6000$.

It is known that, depending on synthesis parameters, two isostructural cubic $Pm\bar{3}m$ phases may coexist in BZY10, i.e., a so-called α -phase (β -phase) with small (large) unit cell and low (high) conductivity.¹⁴ Their peculiar structural difference is the small degree of cross substitution of Y on the Ba sites for the less conducting α -phase.¹⁴ Rietveld refinement of our dry BZY10 NPD data shows that we have 80% β -phase and 20% α -phase for $300 \text{ K} < T < 773 \text{ K}$. The NPD of protonated and deuterated BZY10 reveals low intensity extra Bragg reflections at $Q \sim 4.38, 3.48, 2.78$, and possibly at 2.44 \AA^{-1} (Fig. 2 bottom left panel, shown for deuterated BZY10). The middle panel in Fig. 2 shows a deconvolution of diffracted intensity in the relevant aforementioned Q -ranges, centering on the extra reflections due to deuteration. These reflections are absent in the dry BZY10, revealing that deuteration/protonation creates a long range ordered modulated structure, suggesting that deuterons/protons occupy ordered positions with respect to the crystal lattice.

Transport properties are often influenced by order phenomena. It has been postulated that the oxygen vacancies may order at some particular temperature and then impede ionic transport. The proximity of the Y^{3+} dopant and the oxygen vacancy [Fig. 1(b)] suggests that oxygen vacancy ordering might actually go along with Y^{3+} ordering. At least from the experimental point of view, and because of the peculiar role which Y^{3+} plays in proton conduction, it is then worthwhile to study specifically the Y^{3+} positions, which permits to establish whether Y forms a solid solution with statistical distribution, or whether they are ordered in the lattice. We thus carried out XRD at the Y K -shell absorption edge by taking advantage of the anomalous dispersion of Y and Zr at 17 and 18 keV x-ray energy, respectively. X-ray powder diffractograms of dry BZY10 at 340 K were obtained with different photon energies (Fig. 2, top left panel). At about $Q = 4.49 \text{ \AA}^{-1}$ we notice a peak which seems split at 16 keV, but not at the higher energies. At about this Q value, the (300) and (221) Bragg reflections coincide. Close inspection shows that this peak has actually two shoulders at about $Q = 4.50$ and 4.51 \AA^{-1} , latter of which is apparent as a separate peak at 16 keV, fully 1 keV below the yttrium absorption edge (inset in Fig. 2, top). The intensity in this Q -range has

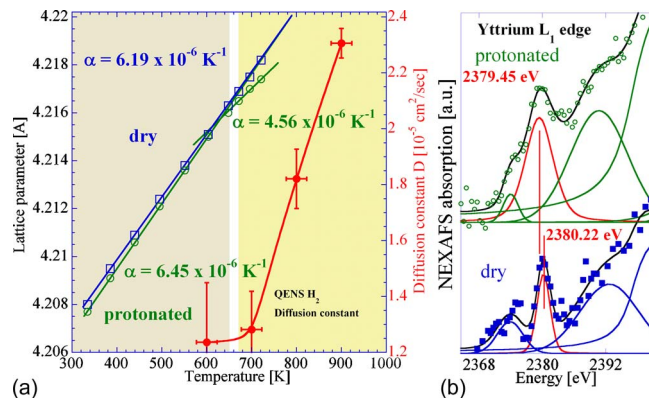


FIG. 3. (Color online) (a) Variation of lattice parameter for dry (blue squares) and protonated/ H_2 loaded (green open circles) BZY10 as function of temperature; errors bars are within symbols. Red dots show the proton diffusion constant as obtained by QENS (temperature error bar derived from thermal gradient between two thermo couples). (b) X-ray L_1 -edge absorption spectra for dry (filled squares) and protonated (open circles) BZY10.

been deconvoluted for the diffractograms of all energies (right panel, Fig. 2) in order to illustrate the three peak positions and the change of their relative intensities. We recall that our BZY10 actually represents two isostructural phases, α and β , with similar lattice constants.¹⁴ Two inequivalent peaks of each phase coincide. Bragg reflections of the cubic ABO_3 perovskites with one even and two odd indices have structure factors proportional to, i.e., $F_{003} = f_B + f_O - f_A$. This is very small for the main phase β in the condition of normal scattering. The multiplicity of equivalent reflections is six, thus the intensity for (003) reads $I_{003} = 6 \times |F_{003}|^2$. Anomalous factors near the absorption edge may have a large effect on the intensity. We briefly exercise this for our ABO_3 -type compound BZY10 with following sites and compositions A: $(1/2, 1/2, 1/2)$, Ba_{1-y} , Y_y ; B: $(0, 0, 0)$, $\text{Zr}_{0.9+y}$, $\text{Y}_{0.1-y}$; and O: $(1/2, 0, 0)$, $\text{O}_{2.95/3}$. The site form factors then read $f_A(Q) = (1-y) \times f_{\text{Ba}}(Q) + y \times f_Y(Q)$; $f_B(Q) = (0.9+y) \times f_{\text{Zr}}(Q) + (0.1-y) \times f_Y(Q)$, and $f_O(Q) = (2.95/3) \times f_O(Q)$. With the tabulated Q -dependent form factors for either element we obtain for the (300) Bragg reflection relative intensities of 104 at 16 keV, 117 at 16.9 keV, 121 at 17 keV, and 59.2 at 25 keV. This intensity variation agrees very well with our experimentally observed (300) intensities in the right part in Fig. 2 (green dominant Voigt distribution). Thus, Y atoms occupy particular lattice positions, and hence likely form an ordered solid solution. These peaks persist also at the higher temperatures. While resolution and statistical robustness of our diffraction are not sufficient to pose one particular, unambiguous crystallographic model with unique lattice positions for Y and H/D, the observed peculiarities do provide evidence for ordering of these species.

Yttrium compounds may present a lattice contraction upon hydrogen incorporation.¹⁵ We observe this for our BZY10, which has at all temperatures studied in the dry state an overall smaller lattice constant than the protonated/deuterated BZY10. The temperature dependent lattice parameters for the β -phase of dry and protonated BZY10 as obtained from Rietveld analysis of the neutron diffractograms are shown in Fig. 3(a) and basically constitute the thermal expansion coefficients α . For the dry β -phase we obtain a linear thermal expansion coefficient of $\alpha = 6.19 \times 10^{-6} \text{ K}^{-1}$. However, the protonated β -phase BZY10 ex-

pands with $\alpha = 6.45 \times 10^{-6} \text{ K}^{-1}$ from 300 K to $648 \pm 20 \text{ K}$, and then with a smaller α of 4.56×10^{-6} from $648 \pm 20 \text{ K}$ to 773 K. The same behavior is observed with the deuterated BZY10, where α was determined to $6.78 \times 10^{-6} \text{ K}^{-1}$ from 300 K to $648 \pm 20 \text{ K}$, and $4.47 \times 10^{-6} \text{ K}^{-1}$ for higher T .

As can be clearly seen in Fig. 3(a), there is a critical transition in the structure of protonated and deuterated BZY10 around $648 \pm 20 \text{ K}$. Interestingly, this transition temperature coincides with the onset of the translational proton transport mode, which was recently measured with quasi-elastic neutron scattering.¹¹ The decreasing slope at $648 \pm 20 \text{ K}$ does not mean that the lattice as such is contracting but that the lattice is expanding less than below this temperature. The fact that the β -phase is the well conducting phase¹⁴ adds confidence to our interpretation that the change in thermal expansion is correlated with the onset of lateral proton diffusion. The right part in Fig. 3(a) (drawn line with filled symbols) shows the proton diffusion constant of protonated BZY10 as a function of T . The data points for $T \geq 700 \text{ K}$ represent the thermal activated proton diffusion by lateral proton jumps, which can be technically exploited in proton conductors. Below 700 K a process with much smaller E_a persists but also with the much smaller proton diffusivity. This process is attributed to the reorientation of the proton around the oxygen, see Fig. 1(d). Because the position of the Bragg reflection of the proton and deuteron does not change during temperature variation, we can also assume that the relative average positions of the protons in the lattice do not change during T variation.

The Y L_1 -shell absorption spectrum of protonated BZY10, recorded at 300 K, is shifted by approximately -0.7 eV compared to dry BZY10, indicating a partial reduction or a charge transfer of the Y upon hydration. The spectrum of dry BZY10 (blue squares in Fig. 3(b)) shows the L_1 absorption peak maximum at 2380.0 eV. This spectrum corresponds to the Y in the setting of Fig. 1(b), where Y is stoichiometrically in the Y^{3+} valence state and exposed to (half of the double negatively charged) oxygen vacancy V_{O} . The peak maximum of the protonated BZY10 (green open circles in Fig. 3(b)) is located slightly below that of the dry BZY10, i.e., at 2379.3 eV, revealing a chemical shift toward a reduced moiety of Y. This corresponds to the situation sketched in Fig. 1(c). The proton does obviously partially reduce yttrium upon hydration, which manifests in the chemical shift of around 0.7 eV toward lower energy. A value of 0.7 eV was found for Sc-doped CaZrO_3 by optical valence band spectroscopy, indicating that the doped protons are exchanged with holes or oxygen vacancies.¹⁶ Mulliken population analysis returns an effective charge of +0.679 electrons for Y in yttrium substituted barium zirconate.¹⁷ Since our spectra were recorded at 300 K, we cannot make any statement on the variation of the oxidation state of Y with increasing T , particularly in the important range at around $648 \pm 20 \text{ K}$ where the proton translational mode and the decrease of the thermal expansion set in. However, our observation of the chemical shift is indirect proof that dissociation of the water molecule sets in at 300 K, and that the proton interacts with the Y ions at ambient T . Because, according to molecular dynamic studies,⁹ the protons barely interact with the oxygen ions, but noticeably interact with the yttrium according to our x-ray absorption spectra, it is difficult to envision the

oxygen ion between the yttrium and the proton. Instead, the protons should be in proximity to the Y. To further test this hypothesis, neutron diffraction measurements with better counting statistics are required. We can speculate over whether at high T the oxygen may leave the lattice; and the cations in BZY10 may become reduced. The smaller thermal expansion at high temperatures for the protonated and deuterated BZY10 may be related with the release of oxygen at high T . The protons need not be in the proximity of the yttrium in order to reduce it, because release of oxygen would cause reduction of the yttrium. In response to that, the protons would be free to leave their position, i.e., become delocalized and thus be available as charge carriers, which basically provide proton conduction. The experiment by Higuchi *et al.*¹⁶ suggests that the electronic structure of proton conductors deserves more attention. Element specific detection techniques like oxygen (1s) x-ray absorption spectroscopy, which can probe the valence band and the hybridization of states, seems particularly promising to solve the question, which role do the oxygen ions play. Such experiments are now in preparation.

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