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Crystal Structure and Proton Conductivity of BaZr0.9Sc0.1O3–δ

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Solid-state sintering has been used to prepare the perovskite BaZr0.9Sc0.1O3–δ. Analysis of X-ray powder diffraction data shows that an increase of the unit cell parameter, a, was observed after deuteration. Rietveld analysis of room-temperature neutron powder diffraction data confirmed cubic symmetry (space group Pm-3m). Dynamic thermogravimetric analysis indicates that the hydration process occurs below 335 °C and approximately 58% of the theoretical number of protonic defects can be filled. The presence of protons/deuterons is seen from the strong O–H/O–D stretch band in the infrared spectrum of the hydrated/deuterated samples. The proton conductivity of a prehydrated sample was investigated under dry and wet Ar atmospheres.

I. Introduction

Electrolyte materials are generally ionic conductors and electronic insulators. Proton conducting electrolytes have a wide range of potential applications in fuel cells, batteries, sensors, electrolysers, etc.1–3 Among these application fields, the most promising and time-relevant use of these materials is in fuel cells. For example, in low-temperature (T<100°C) fuel cells such as a polymer electrolyte fuel cell (PEFC), Nafion (perfluorosulfonic polymer) is used as the electrolyte material, with the low operating temperatures necessitating the use of expensive platinum catalysts. Currently, high-temperature fuel cells based on oxide-ion conductors operate at T>600°C, which limits the wide range of materials selectivity and also leads to slow start-up intervals. Therefore, a proton conducting fuel cell operating in the intermediate temperature range (200°C–600°C) is a desirable alternative.

Successive investigation and literature data compiled by Norby2 show the presence of a “gap,” within the intermediate temperature range, in which no materials show sufficiently high proton conductivity. Narrowing this gap would be very beneficial from a technological point of view. For A2B+2O3-type perovskite oxides, Y-doped BaZrO3 and BaCeO3 show the highest proton conductivities.4–10 Different parameters, such as hydration enthalpy (ΔH), electronegativity, size of the dopant atoms, and crystal structure, have been used in order to understand the material conduction properties and predict new materials that may exhibit high conductivity. In A2B+2O3-type perovskite oxides, such as Li0.2Sr0.1Mo3–δ (M = Sc, In, and Lu), the highest proton conductivity was found in the Sc compound,11 i.e. in the materials with the smallest B-site cation. A different dependence was observed for the A2B+2O3-type perovskite oxides of BaZr0.95M0.05O3–δ (M = Y, Dy, In, Nd, and Ga).12 Here, it was reported that the proton conductivity increased with an increase in dopant B-site cation size up to an ionic radius of ≈0.9 Å and when the ionic radius of the dopant ion exceeds 0.9 Å, the conductivity starts to decrease, for example for Nd. For complex perovskites, higher conductivity and lower activation energy are generally found when the difference in the ionic radius of the B-site cations is small.13 Indeed, the factors controlling the conduction process may be different for different types of perovskite oxides. In addition, enhanced conductivity is usually observed for A-site cations of higher ionic radius.5,12 In general, the sample having a higher crystal symmetry shows higher proton conductivity; this is especially true for zirconate systems.

In this study, 10 mol% Sc-doped BaZr0.975Y0.025O3 was investigated. Proton diffusivity in this material has been investigated before at low temperatures, T≤200°C.14 In the present study, we have used a combination of different techniques: X-ray powder diffraction (XRPD), neutron powder diffraction (NPD), dynamic thermogravimetric analysis (TG), infrared (IR) spectroscopy, and electrochemical measurements (impedance analysis). Deuterium-substituted samples have been used in the NPD experiments due to the high incoherent neutron scattering cross section of protons.

II. Experimental Procedure

Samples were prepared by a traditional solid-state sintering technique. Appropriate amounts of BaCO3 (99.9%), SrCO3 (99.9%), and ZrO2 (<2% HfO2) have been mixed in order to obtain the desired compositions. The oxides were heated to 800°C overnight to remove moisture before weighing. To ensure thorough mixing, ethanol (99.5%) was added during the milling, which was performed manually using an agate mortar and pestle. The finely ground material was fired at 1000°C for 8 h and subsequently ground and pelleted using a 13 mm diameter die under a pressure of ≈538 MPa (8 tons). The pellets were sintered at 1200°C in air for 72 h and finally reground and compacted under similar conditions and refired at 1500°C for 48 h. The amount of HF in the sintered powder was investigated by inductively coupled-plasma (ICP) emission spectroscopy. The ICP result showed that 1 mol% of HF was present in the sintered powder and this value has been used as a starting value for Rietveld refinement, which is described in the discussion. After sintering at 1500°C, the pellets showed a density corresponding to ≈70% of the theoretical value. A dried sample was prepared by annealing the as-prepared sample at 900°C in ≈10–6 mbar

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N.J. Dudney—contributing editor
pressure. The hydration reaction was carried out at 300 °C under a humid atmosphere (N₂ saturated with water vapor at 76.2 °C, i.e. P(H₂O) = 0.40 atm) for several days.

The XRPD measurements were carried out at ambient temperature using a Siemens D5000 powder diffractometer (Bruker-AXS, Karlsruhe, Germany) (CuKα = 1.5418 Å). For structural refinement, the XRPD data (in this case, a Bruker AXS D8 ADVANCE VARIO powder diffractometer, CuKα1 = 1.54058 Å, was used) were collected over a 2θ range of 15°–120° with a step size of 0.02° and an acquisition time per step of 15 s.

The TREOR program was used for indexing and evaluation of the lattice parameter. NPD data for dried and deuterated samples were collected at ambient temperature on a high-resolution D2B diffractometer with a λ = 1.5937 Å (at the Institut Laue Langevin, Grenoble, France). The obtained data sets were refined using the Rietveld method using the GSAS (for analysis of NPD data) and Fullprof software.

Dynamic TGA was carried out on a dried sample on heating from 65° to 925 °C as well as cooling from 925° to 65 °C with a Setaram TAG 16 using a rate of 1.5 °C/min. The measurement was performed under a stream of Ar gas saturated with water vapor at 46 °C (P(H₂O) = 0.10 atm) with a flow rate of 20 mL/min.

The IR experiments were performed in an inert Ar atmosphere at room temperature in the diffuse reflectance mode using a Bruker VECTOR 22 FTIR spectrometer, equipped with a KBr beamsplitter, a deuterated triglycerine sulfate detector, and a diffuse reflectance device (Graseby Specac, "Selector"). A wrinkled aluminum foil was used as a reference. The vibrational spectra was derived by taking the logarithm of the ratio between the reference spectrum and the sample spectrum.

The impedance was measured from 1 MHz to 1 Hz using a Solaron 1260 frequency response analyzer in the stand-alone mode. The sine wave amplitude was 1 V rms. The conductivity cell used was a ProboStat from Norwegian Electro Ceramics AS (NorECs). Approximately 0.3 cm² of the oxide electrode surface was covered with a conducting platinum paste and a platinum grid to assure good ohmic contacts. The covered surface area was measured using an optical microscope. At first impedance measurements were performed for prehydrated samples on heating from 150° to 900° C (heating cycle) and down from 900° to 150 °C (cooling cycle) under a dried Ar atmosphere at 50 C intervals and allowing 10 min to elapse at each new temperature before the impedance was recorded. In this case, the Ar gas was dried by flowing through two beds of P₂O₅. In order to limit any water uptake from the ambient atmospheres, two silica tubes were used to encase the cell as extra protection during the experiments. Wet runs were subsequently carried out with a porous Al₂O₃ outer tube on the same pellet under Ar saturated at 22 °C with water, or heavy water vapor, (P(H₂O) or P(D₂O) = 0.026 atm) on cooling from 900° to 150° C in 50 °C steps. After reaching the desired temperature, 1 h elapsed before the impedance spectra were recorded.

Two or three time constants were generally observed for all runs (except cooling cycle of the prehydrated sample under dry Ar), corresponding to the bulk and grain boundary conduction. A typical complex plane plot is shown in Fig. 1, together with the equivalent circuit used in the data analysis. The obtained capacitance values were ≈10⁻¹¹ F cm⁻² for bulk conductivity and ≈10⁻⁸ F cm⁻² for grain boundary conduction. Beyond 300 °C, it was difficult to separate the different conduction processes for all runs. Only one time constant was observed during the cooling cycle of the prehydrated sample and in this case one resistance—capacitance (RC) parallel equivalent circuit (constant phase elements [CPE] instead of a pure capacitor) was used to evaluate the impedance spectra.

### III. Results

The room-temperature XRPD patterns of dried and deuterated BaZr₀.₉Sc₀.₁O₃₋₈ are shown in Fig. 2. Indexing of these patterns clearly indicates that all samples possess cubic symmetry of space group Pm₃m. The unit-cell parameters (a) have been determined from XRPD to be 4.1908(1) Å and 4.1946(4) Å for dried and deuterated samples, respectively. A similar value (a: 4.19276(6) Å) was reported by Kreuer et al. Figure 3 plots the Rietveld fit achieved to XRD data for the as-prepared sample and Figs. 4 and 5 show the NPD data collected for dried

![Fig. 1. Complex plane plot of BaZr₀.₉Sc₀.₁O₃₋₈. Inset shows equivalent circuit used to extract the impedance data.](image1)

![Fig. 2. X-ray diffraction patterns of dried and deuterated BaZr₀.₉Sc₀.₁O₃₋₈. *Represents the peaks due to silicon used as calibration standard. After deuteration the corresponding single peak shifts towards lower 20 value (see the inset).](image2)

![Fig. 3. Observed room temperature X-ray powder diffraction profile of as-prepared BaZr₀.₉Sc₀.₁H₀.₁O₀.₈5 (points), calculated pattern (solid line) and difference line (bottom). The tick marks show the positions of the Bragg peaks predicted by the structural model. Inset clearly shows no indication of impurities.](image3)
and deuterated samples, respectively. A summary of the information obtained from the Rietveld structural analyses is shown in Table I. We refined the fractional occupancy (both for XRPD and NPD data) of the A-site cation in order to check for the presence of any Ba deficiency that may have arisen from the high sintering temperature (1500°C for 48 h). The refined A-site occupancy did not show any tendency to decrease from unity, i.e. values of 1.002(3) and 1.071(6) were obtained from the XRPD and NPD refinements, and therefore this value was set to 1.00. In contrast, the refinement of the B-site cations (fractional occupancies and isotropic atomic displacement parameter (IADP) for XRPD and NPD data) and oxygen occupancies and IADP (only for NPD data) converged rapidly, producing significant improvements to the quality of fit and chemically sensible values. The fractional occupancy and IADP of the oxygen site could not be obtained reliably from the XRPD data and consequently they were fixed to sensible values of 0.983(3)/C2.5 and 2.5 Å², respectively.

According to our previous investigation of a closely related acceptor-doped perovskite, deuterium ions are found close to the oxygen site on the Wyckoff 12h positions (1/2, 0.2, 0) or possibly the 24k positions (0.54, 0.21, 0) within Pm–3m symmetry. We used similar starting values for the analysis of the data from the deuterated BaZr0.9Sc0.1O3d sample in our attempts to locate deuterium ions within the structure. However, the refined deuterium position and site occupancy did not converge well enough to draw any definite conclusions.

Figure 6 shows the dynamic TGA result for the dried sample under a humid condition (10 vol% water vapor). A change in mass was monitored during a heating and cooling run under a similar condition. During the heating cycle, mass gain occurred below 335°C, while mass loss started beyond 335°C. Above 800°C, no mass change was observed. During the cooling cycle below 800°C, the sample starts to gain mass under the same humid atmosphere. Finally, the sample regains its original mass approximately, which confirms the reversibility of the hydration process. The reversible mass loss/gain under a humid atmosphere was 0.19 wt%, which suggests that approximately 58% of the theoretically possible protonic defects [OH−] in BaZr0.9Sc0.1O3d were filled.

The infrared spectra of the hydrated, deuterated, and the dried samples are shown in Fig. 7. The spectrum of the hydrated sample shows a strong O–H stretch band, typical of hydrated perovskites.5,21,22 This confirms the presence of dissolved protons into the perovskite structure of BaZr0.9Sc0.1O3d after hydration. Here, we also note that the spectrum of the dried sample contains a weak O–H stretch band, which also indicates the presence of some protons in the dried samples although the

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**Table I. Summary Rietveld Analysis for BaZr0.9Sc0.1O3d**

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Space Group</th>
<th>Lattice Parameter</th>
<th>Thermal Parameter</th>
<th>Occupancies</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared sample</td>
<td>Pm–3m</td>
<td>4.1952(1) Å</td>
<td>Biso(Å²)</td>
<td>Ba 1.0</td>
</tr>
<tr>
<td>Dried sample</td>
<td>Pm–3m</td>
<td>4.1881(1) Å</td>
<td>0.71(3)</td>
<td>Zr 0.891(2)</td>
</tr>
<tr>
<td>Deuterated sample</td>
<td>Pm–3m</td>
<td>4.1914(1) Å</td>
<td>0.79(2)</td>
<td>Hf 0.009 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sc 0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O 0.983</td>
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<td></td>
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<td>Weighted $R$ factor(%)</td>
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<td>Expected $R$ factor(%)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>No of fitted 15 parameters</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Both X-ray and neutron powder diffraction data were collected at ambient temperature.
amount is considerably smaller than in the hydrated sample. For the deuterated sample, the spectrum shows the presence of both deuterons and protons in the structure as the band between 2000 and 2500 cm$^{-1}$ is related to O–D stretches.

Figure 8 shows the Arrhenius plots of conductivity for the prehydrated sample under dry and wet Ar atmospheres. The total conductivity measured under a heavy water (D$_2$O) atmosphere was lower (Fig. 8) compared with under a water (H$_2$O) atmosphere under different experimental conditions.

Furthermore, refinement of Ar prehydrated sample under dry and wet Ar atmospheres. The Rietveld analysis of both the NPD and long scan (15.5 h) XRPD data did not show any indication of extra peaks arising from Rietveld analysis (Table I) of the NPD data confirms the cubic crystal symmetry and space group for both dried and deuterated samples. An expansion of the unit cell is often observed after hydration/deuteration.20,26–29 This expansion of the unit cell parameter is a result of filling of oxygen vacancies (V$^{\text{O}}_\text{O}$) by hydroxyl groups (OH$_2^-$/OD$_2^-$) in the presence of water or heavy water vapor according to the following reaction:

$$\text{D}_2\text{O}/\text{H}_2\text{O}(g) + \text{O}_\text{O}^+ + V^{\text{O}}_\text{O}^\text{\textdagger} \leftrightarrow 2\text{OD}_\text{O}^\text{\textdagger}/2\text{OH}_\text{O}^\text{\textdagger}$$

Rietveld analysis (Table I) of the NPD data confirms the cubic crystal symmetry and space group for both dried and deuterated samples. An expansion of the unit cell of the deuterated sample was also confirmed from the Rietveld analyses. In order to improve the electrical conductivity of the sample, charge-compensating oxygen vacancies (V$^{\text{O}}_\text{O}$) were created by partial substitution of trivalent Sc for tetravalent Zr ions. Charge balance calculations based on the idealized stoichiometry of BaZr$_{0.9}$Sc$_{0.1}$O$_{3-\delta}$ indicate that a maximum of 0.05 moles of oxygen vacancy (V$^{\text{O}}_\text{O}$) “per chemical formula” can be formed in the dried sample. Our refined oxygen content from the NPD data analysis for the dried sample showed that 0.04(1) moles of V$^{\text{O}}_\text{O}$ were in fact obtained, confirming that charge compensation occurred via vacancy formation. In an oxidizing atmosphere, charge compensation may instead occur through the formation of electronic holes as reported elsewhere.30–32 The oxygen content refined for the deuterated sample was O$_{3.02}$, i.e., the oxygen vacancies were as expected, filled by O–D groups according to reaction 1. Hence, the refined oxygen levels for both samples were in good agreement with expected values of O$_{2.95}$ and O$_{1.96}$ for dried and deuterated samples, respectively.

The deuterium positions were not successfully located within the structure of the deuterated sample. For a 10 mol% Sc$^{3+}$-substituted BaZrO$_3$ sample, full occupation of the oxygen sites, and corresponding incorporation of twice as many deuterium (D) ions, would lead to a maximum of only 0.1 mol D/mol of BaZr$_{0.9}$Sc$_{0.1}$O$_{2.95}$. At such low deuterium concentrations, it is quite difficult to locate their position reliably. Moreover, at ambient temperatures, the deuterium ions rotate around the oxide ions and are not fixed at one position.33 As suggested by Knight,34 a higher doping, which corresponds to a higher concentration of D in the structure, is required to obtain accurate refinement of deuterium positions, thermal parameters, and site occupancies. However, utilization of high-resolution NPD data collected at a low temperature can also be valuable. This is an approach that has already been successfully used to locate D sites for deuterated BaZr$_{0.9}$In$_{0.1}$O$_{3-\delta}$ at 5 K by Ahmed et al.,20 SrZr$_{0.5}$In$_{0.5}$O$_{3-\delta}$ at 10 K by Ito et al.,35 and for protonated BaCe$_{0.5}$Y$_{0.5}$O$_{2.95}$ at 4.2 K by Knight.34

The result of the dynamic TGA shows that the content of protons in the title compound was less (58% of the theoretical value) compared with for example, 10 mol% Yb-doped (74% of the theoretical value) under identical conditions. In order to explain this result, the enthalpy of the hydration reaction (Eq. (1)) $\Delta H$ was calculated using the equation reported by Norby et al.,36 where,
proton uptake is easily possible at these temperatures as the kinetics of the water uptake reaction is believed to be fast. However, the difference in conductivity becomes smaller at temperatures >800°C. At such high temperatures, the protonic defects are unstable in the material; hence, protons are not the dominating charge carriers. Possibly oxide-ion or hole conduction dominates in the high-temperature range.

Lower conductivity (Fig. 8) under heavy water (D₂O + Ar) compared with under water (H₂O + Ar) in the temperature range 150–600°C in fact shows the isotope effect, which, in principle, confirms that the material is a proton conductor. The classical isotope effect expected for the conductivity measurement is that \( \sigma_{D}/\sigma_{H} \approx \sqrt{2} \). In this study, the ratio \( \sigma_{\text{D}}/\sigma_{\text{H}} \) (for bulk) was \( \approx 2.5–3 \) and \( \sigma_{\text{D}}/\sigma_{\text{H}} \) (for total) was \( \approx 1.4–1.5 \). Survey of conductivity results on other perovskite oxides reveals that similar values were also reported by Nowick and Vaysleb. From Fig. 8, it is apparent that somewhat higher activation energies were obtained compared with the typical values of \( \sim 0.4–0.5 \) eV found for the best proton conductors such as Y-doped BaZrO₃ and BaCeO₃.\(^{12,39}\) Islam et al.\(^{42}\) calculated that the binding energies of hydroxyp-dopant pairs (OH\(^\text{−}\)/M\(_{Zr}\)) were \( \sim 0.74 \) eV and \( \sim 0.26 \) eV, for \( M = Sc \) and \( Y \), respectively. In addition, higher interaction energies (\( \Delta E_{\text{int}} \)) for dopant–proton clusters in BaZrO₃ were reported for the case of a Sc dopant compared with a Y dopant.\(^{43}\) According to recent first principle investigations of BaZrO₃ by Björketun et al.,\(^{46}\) it was found that the dopants act as “trapping” centers for migratory protons. This trapping region was strongly correlated with dopant radius. Our experimental findings show good agreement with theoretical work, confirming a higher activation energy and lower proton mobility for Sc-doped BaZrO₃. Similar experimental results for the temperature interval below 200°C have also been reported by Kreuer et al.\(^{14}\)

V. Conclusions

Using a standard solid-state synthesis route, it was possible to obtain single-phase BaZr\(_{0.9}Sc_{0.1}O_{3−δ}\) samples. Analysis of XRPD and NPD data indicates that the structure of all the samples show cubic symmetry (space group \( Pm\text{̅}m \)). Dynamic TGA data showed that nearly 58% of the theoretical number of protonic defects can be filled upon hydration. IR spectra clearly show the presence of a significant number of protons in the hydrated sample compared with the dried sample. Proton conduction in this material was mainly dominating in the temperature range (150–600°C). The lower proton conductivity and higher activation energy reflects a strong association between the proton and the Sc-dopant ions, in agreement with several theoretical studies.

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