Supplemental Information for:

Dynamic Nuclear Polarization NMR of Low Gamma Nuclei: Structural Insights into Hydrated Yttrium-doped BaZrO$_3$

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1. Materials and Methods

Materials

Y-doped BaZrO$_3$ samples (Table S1) were prepared using a chemical solution method.$^1$ Compacts were prepared by isostatic pressing and these were sintered at 1580 °C for 24 hours under flowing air to obtain samples of greater than 92% theoretical density. The samples were hand crushed, sieved and then hydrated in a tube furnace using a literature procedure.$^{1,2}$

Table S1. Nominal composition and particles size of the samples used.

<table>
<thead>
<tr>
<th>Samples</th>
<th>% mol Y</th>
<th>Composition</th>
<th>Particles size (µm) $^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BZY20</td>
<td>20</td>
<td>BaZr$<em>{0.8}$Y$</em>{0.2}$(OH)$<em>{0.07}$O$</em>{3-\delta}$</td>
<td>d &lt; 45</td>
</tr>
<tr>
<td>BZY30</td>
<td>30</td>
<td>BaZr$<em>{0.7}$Y$</em>{0.3}$(OH)$<em>{0.09}$O$</em>{3-\delta}$</td>
<td>d &lt; 45</td>
</tr>
<tr>
<td>BZY40</td>
<td>40</td>
<td>BaZr$<em>{0.6}$Y$</em>{0.4}$(OH)$<em>{0.12}$O$</em>{3-\delta}$</td>
<td>45 &lt; d &lt; 75</td>
</tr>
</tbody>
</table>

DNP enhanced MAS NMR spectroscopy

The Y(NO$_3$)$_3$ samples for the DNP experiments were prepared by dissolving Y(NO$_3$)$_3$·4H$_2$O in a 12 mM AMUPol$^3$ biradical solution in either d$_6$-DMSO/H$_2$O (60/40 volume %) or d$_8$-glycerol/D$_2$O/H$_2$O (60/30/10 volume %) to yield an Y$^{3+}$ concentration of 0.5 M. 20 µL of the solution was added to a sapphire rotor, capped with a silica insert (seen at 0 ppm in the $^1$H spectra) and a zirconia drive tip, and inserted into the DNP NMR probe.$^4$

The BZY samples for the DNP experiments were prepared by wet impregnation using d$_6$-DMSO/H$_2$O solution, unless otherwise specified. Typically, the BZY samples ($\approx$ 60 mg) were wet with 20 µL of 12 mM of AMUPol$^3$ biradical solution in d$_6$-DMSO/H$_2$O (60/40 volume %). This mixture was quickly stirred, centrifuged into a sapphire rotor, capped with a polyfluoroethylene plug and a zirconia drive tip, and inserted into the DNP NMR probe.$^4$ One sample of BZY30 was prepared similarly using 30 µL of 10 mM of bCTbK$^{5,6}$ biradical solution in 1,1,2,2-tetrabromoethane.$^7$

All solid-state NMR experiments were performed on a commercial 9.4 T Bruker Avance III DNP solid-state NMR spectrometer equipped with a 263.7 GHz gyrotron microwave system.
All NMR experiments were recorded with a 3.2 mm HXY triple-resonance MAS probe\(^3\) (in \(\lambda/4\) transmission mode) at \(v_0(\text{H}) = 400.26\) MHz corresponding to the maximum enhancement proton position \(\varepsilon_H\) for TOTAPOL at \(v_0(e^-) = 263.7\) GHz, with the X channel tuned to \(^{13}\text{C}\) at \(v_0(^{13}\text{C}) = 100.60\) MHz and Y channel tuned to \(^{89}\text{Y}\) at \(v_0(^{89}\text{Y}) = 19.62\) MHz. A home adapted triple resonance \(^1\text{H}\) \(^{13}\text{C}\) \(^{89}\text{Y}\) circuit was constructed consisting of a 15 pF capacitor in parallel to an insert coil of 7 turns, used to bridge the X and Y channels, and also a 142 pF ‘shunt’ capacitance in parallel to the variable Y capacitor. The Y channel tuning range at low temperature (~ 100 K) using this setup is 19.7 ± 0.2 MHz. All \(^1\text{H}\) and \(^{89}\text{Y}\) experiments were performed under magic angle spinning (MAS) at \(\nu_r = 8\) and 5 kHz, respectively, and at \(T \approx 105\) K. All \(^1\text{H}\) short pulses, FSLG homonuclear decoupling\(^8\) and SPINAL-64 heteronuclear decoupling\(^4\) were performed at a radio-frequency (rf) field amplitude of \(v_1(^{1}\text{H}) = 100\) kHz. All \(^1\text{H}^{89}\text{Y}\) CP MAS experiments were obtained with a \(^{89}\text{Y}\) rf field of \(v_1(^{89}\text{Y}) = 25\) kHz, while the \(^1\text{H}\) rf field amplitude was ramped to obtain maximum signal at a \(^1\text{H}\) rf field of \(v_1(^{1}\text{H}) = 30\) kHz. The contact time \(\tau_{\text{CP}}\) is given in the figure captions. All acquisitions started with saturation pulses, consisting of a train of 50 \(^1\text{H}\) \(\pi/2\) pulses of 2.5 \(\mu\)s separated by 1 ms, to ensure elimination of any residual \(^1\text{H}\) magnetization under our experimental conditions. The build-up times in the absence and presence of microwave irradiation, which are characterized by different time constants \(T_1\) and \(T_B\), respectively, were obtained with saturation recovery experiments (Table S2). The recycle delays were set equal to or longer than 1.3 x \(T_1\) for microwave off experiments and 1.3 x \(T_B\) for microwave on experiments. \(^{89}\text{Y}\) chemical shifts were externally referenced at room temperature to the most intense resonance of \(\text{Y}_2\text{O}_3\) (doped with 1 % Gd) at 330 ppm, and are given at ± 8 ppm.
Table S2. Values of $^1$H DNP enhancement $\varepsilon(^1\text{H})$, $^1$H build-up polarization times $T_B$ and $T_1$, and $^{89}$Y CP DNP enhancement $\varepsilon(^{89}\text{Y CP})$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\varepsilon(^1\text{H})^a$</th>
<th>$T_B$ / s $^b$</th>
<th>$T_1$ / s $^b$</th>
<th>$\varepsilon(^{89}\text{Y CP})^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M Y(NO$_3$)$_3$ with 12 mM AMUPol in 60/40 (v/v) d$_6$-DMSO/H$_2$O</td>
<td>15</td>
<td>0.4/3.1</td>
<td>0.4/2.0</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>0.5 M Y(NO$_3$)$_3$ with 12 mM AMUPol in 60/30/10 (v/v) d$_6$-glycerol/D$_2$O/H$_2$O</td>
<td>100</td>
<td>0.5/4.4</td>
<td>0.4/4.8</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>BZY20 wetted with 12 mM AMUPol in 60/40 (v/v) d$_6$-DMSO/H$_2$O</td>
<td>10</td>
<td>4.0/31.3</td>
<td>2.8/35.6</td>
<td>3</td>
</tr>
<tr>
<td>BZY30 wetted with 12 mM AMUPol in 60/40 (v/v) d$_6$-DMSO/H$_2$O</td>
<td>9</td>
<td>2.4/13</td>
<td>3.1/17.7</td>
<td>2</td>
</tr>
<tr>
<td>BZY30 wetted with 12 mM AMUPol in 60/30/10 (v/v) d$_6$-glycerol/D$_2$O/H$_2$O</td>
<td>196</td>
<td>3</td>
<td>3/14.6</td>
<td>1.5</td>
</tr>
<tr>
<td>BZY30 wetted with 10 mM bCTbK in C$_2$Br$_3$H$_2$</td>
<td>28</td>
<td>3.6</td>
<td>3.3/18.6</td>
<td>~ 1</td>
</tr>
<tr>
<td>BZY40 wetted with 12 mM AMUPol in 60/40 (v/v) d$_6$-DMSO/H$_2$O</td>
<td>10</td>
<td>-</td>
<td>5.0/16</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ DNP measurements at $\nu_0(\varepsilon) = 263.7$ GHz ($\nu_0(^1\text{H}) = 400.26$ MHz), 105 K, $\nu_r = 8$ kHz. $^b$ Polarization build-up times $T_B$ and $T_1$ were measured with saturation recovery experiment with and without microwave irradiation, respectively. Two values are given when the build-up curve is best described with two time constants. $^c$ DNP measurements at $\nu_0(\varepsilon) = 263.7$ GHz ($\nu_0(^1\text{H}) = 400.26$ MHz and $\nu_0(^{89}\text{Y}) = 19.61$ MHz), 105 K, $\nu_r = 5$ kHz.

2. Computational Methods

Energetics and Configurations

First principles periodic solid-state density functional theory (DFT) calculations were carried out using the CASTEP code,$^9$ providing total energies, optimized structures and NMR parameters for configurations considered, and are similar to recent studies.$^{10-14}$ This combines a plane-wave basis set with the total energy pseudo-potential method and is ideal for periodic systems. The Perde-Burke-Ernzerhof GGA-type (generalized-gradient approximation) exchange-correlation functional was used throughout.$^{15}$ Cell parameters and atomic positions of various configurations were fully geometrically optimized using a basis set cutoff of 50 Ry (680 eV) and without any symmetry constraints. A Monkhorst-Pack$^{16}$ k-point mesh of $3 \times 3 \times 3$ was used.
along with total energy, force, displacement and stress convergence tolerances of $1 \times 10^{-6}$ eV, $1 \times 10^{-3}$ eV Å$^{-1}$, $1 \times 10^{-3}$ Å, $5 \times 10^{-3}$ GPa, respectively.

Calculations based on hydrated yttrium doped barium zirconate (space group $Pm\overline{3}m$) containing 12.5% yttrium as a dopant $[\text{BaZr}_{1-x}\text{Y}_x\text{O}_{3-x}x(\text{OH})_x, x = 0.125]$ were considered, and $2 \times 2 \times 2$ supercells were constructed. One Zr was replaced by a trivalent Y dopant and one proton was attached to a lattice oxygen forming a hydroxyl group, leading to supercells with 41 atoms and a composition of $\text{Ba}_8\text{Zr}_7\text{YO}_{24}x$. The number of considered configurations relies upon the number of available proton sites around the lattice oxygen to which it is bound. It has been demonstrated for perovskites with large lattice constants, such as $\text{SrZrO}_3^{17}$ and $\text{BaCeO}_3^{18-21}$ (pseudocubic lattice constant $a_0 = 4.14$ and 4.41 Å, respectively), that O-H bonds orient along the pseudocubic direction, leading to four possible protonic sites per oxygen atom.$^{21}$ This leads to 96 available protonic sites within the supercell, however, through symmetry operations this reduces to four unique configurations (Figure S9): ‘near’, the proton is attached to an oxygen next to yttrium; ‘planar’, the proton is on the next nearest oxygen with the hydroxyl group orientated within the plane containing yttrium; ‘perpendicular’, the proton is on the next nearest oxygen with the hydroxyl group orientated out of the plane containing yttrium; ‘distant’, the proton is attached to an oxygen furthest from the yttrium. This also allows the influence of the Y dopant on the energetic minima of the protonic energy landscape to be monitored in relation to proton-dopant distance (Figure S10).

**NMR Calculations**

NMR parameters were obtained from fully geometrically optimized configurations with the GIPAW approach.$^{22,23}$ Calculated isotropic magnetic shieldings ($\sigma_{\text{iso}}$) were converted to isotropic chemical shifts ($\delta_{\text{iso}}$) to allow for comparison with experiments. The following expression was used for $^{89}\text{Y}$: $\delta_{\text{iso}}(^{89}\text{Y}) = 2385.30 - 0.8945 \sigma_{\text{iso}}(^{89}\text{Y})$, based on results obtained
from Reader et al.\textsuperscript{24} A mean absolute error (MAE) of 15 ppm was obtained for \textsuperscript{89}Y relative to experiment. The expression used for \textsuperscript{1}H was $\delta_{\text{iso}}(^{1}\text{H}) = 28.45 - 0.93 \sigma_{\text{iso}}(^{1}\text{H})$ with a MAE of 0.29 ppm (unpublished results).

Details of projector augmented wave sets used

H: 1|0.8|0.8|0.6|2|6|8|10(qc=6)

O: 2|1.0|1.3|0.7|13|16|18|20:21(qc=7)

Y: 3|2.0|2.0|2.0|7|9|10|40U:50U:41:42

Zr: 3|2.1|2.1|1.8|7|9|10|40U:50U:41:42

Ba: 2|3.0|2.9|2.2|2|3|5|50U:60:51U2.5U2.5(qc=3.5)
3. Figures

![Figure S1](image)

**Figure S1.** $^1$H MAS spectra of 0.5 M Y(NO$_3$)$_3$ with (a) 12 mM AMUPol in 60/40 (v/v) d$_6$-DMSO/H$_2$O and (b) 12 mM AMUPol in 60/30/10 (v/v) d$_8$-glycerol/H$_2$O/D$_2$O recorded with (green) and without (red) microwave irradiation at $\nu_0(e^-) = 263.7$ GHz. 4 scans were recorded. The DNP enhancements were determined as $\varepsilon = A_{\text{DNP}}/A_{\text{Boltzmann}}$ where $A_{\text{DNP}}$ and $A_{\text{Boltzmann}}$ are the signal areas with and without microwave irradiation, respectively.
Figure S2. $^{89}$Y CP MAS spectra of BZY20 recorded with microwave irradiation at $v_0(e^-) = 263.7$ GHz as function of the CP contact time $\tau_{CP}$. The sample was wet with 12 mM AMUPol in $60/40$ (v/v) $d_6$-DMSO/H$_2$O. 64 scans were recorded.
Figure S3. $^1$H MAS spectra of (a) BZY20, (b) BZY30 and (c) BZY40 recorded with (green) and without (red) microwave irradiation at $\nu_0(e^-) = 263.7$ GHz. The samples were wet with 12 mM AMUPol in 60/40 (v/v) d$_6$-DMSO/H$_2$O. 4 scans were recorded.
Figure S4. (a) $^1$H MAS and (b) $^{89}$Y CP MAS spectra of BZY30 recorded with (green) and without (red) microwave irradiation at $v_0(e^-) = 263.7$ GHz. The sample was wet with 12 mM AMUPol in 60/30/10 (v/v) d$_8$-glycerol/D$_2$O/H$_2$O. In (a), 4 scans were recorded. In (b) 128 scans were recorded and the CP contact time was 20 ms. $\varepsilon(^1H)$ and $\varepsilon(^{89}Y$ CP) were determined by comparing the corresponding spectra with and without microwave irradiation, and were 196 and $\sim1.5$, respectively.
Figure S5. (a) $^1$H MAS and (b) $^{89}$Y CP MAS spectra of BZY30 recorded with (green) and without (red) microwave irradiation at $\nu_0(e^-) = 263.7$ GHz. The sample was wet with 10 mM bCTbK in 1,1,2,2-tetrabromoethane. In (a), 4 scans were recorded. In (b) 128 scans were recorded and the CP contact time was 20 ms. $\varepsilon(^1\text{H})$ and $\varepsilon(^{89}\text{Y CP})$ were determined by comparing the corresponding spectra with and without microwave irradiation, and were 28 and $\sim 1$, respectively.
Figure S6. $^1$H $^{89}$Y CP MAS spectra of BZY40 recorded with (green) and without (red) microwave irradiation at $\nu_0(e^-) = 263.7$ GHz. 64 scans were recorded and the CP contact time was 20 ms. The sample was wet with 12 mM AMUPol in 60/40 (v/v) $d_6$-DMSO/H$_2$O. $\varepsilon(\text{$^1$H})$ and $\varepsilon(\text{$^{89}$Y CP})$ were determined by comparing the corresponding spectra with and without microwave irradiation, and were 10 and $\sim 1$, respectively.

Figure S7. $^1$H MAS spectrum of BZY40 obtained under $\nu_{\text{rot}} = 8$ kHz at $\sim 100$ K without polarizing agents and solvents.
Figure S8. Contour plot of the two-dimensional $^1$H $^{89}$Y CP MAS HETCOR spectra of BZY30 recorded under microwave irradiation at $v_0(e^-) = 263.7$ GHz. The sample was wet with 12 mM AMUPol in 60/40 (v/v) $d_6$-DMSO/H$_2$O. All the others acquisition parameters and sample details are identical to Fig. 2. A total of 32 $t_1$ increments of 36 $\mu$s with 64 scans and a 23 s recycle delay were acquired (experimental time = 13 h). Top: $^1$H $^{89}$Y CP MAS spectra (320 scans accumulated). Left: $^1$H MAS spectrum obtained under $v_{rot} = 8$ kHz at $\sim 100$ K of BZY30 without polarizing agents and solvents.
4. Discussion of the DFT calculations

Optimized Structures and Energetics

The four model configurations for hydrated 12.5 % doped yttrium doped BaZrO$_3$ [BaZr$_{1-x}$Y$_x$O$_{3.5}$x(OH)$_x$, x = 0.125] were geometrically optimized with final geometries shown in Figure S8. Severe lattice distortions are present in the optimised geometries, which manifest itself by the displacement of lattice oxygens leading to non-linear M-O-M bonds and rotations of MO$_6$ octahedra (M = Y, Zr). Further details of local lattice distortions are given below.

![Figure S8.](image)

**Figure S9.** Fully geometrically optimized structures of BaZr$_{1-x}$Y$_x$O$_{3.5}$x(OH)$_x$ (x = 0.125) for four different OH group configurations: (i) ‘near’, (ii) ‘planar’, (iii) ‘perpendicular’, (iv) ‘distant’, (a) ball-and-stick model of 2 × 2 × 2 supercells, (b) polyhedral model of the hydrogen bond plane. Zirconium, yttrium, oxygen and hydrogen atoms are in blue, purple, red and white, respectively. Barium atoms have been omitted for clarity.

The final energies of all the configurations described above are taken from single point calculations and compared in Figure S10. This provides a method of comparing energy minima values across the supercell energy landscape as a function of proton-dopant separation. The path of the proton from ‘near’ to ‘distant’ shows an increase of ~ 24 kJ.mol$^{-1}$, demonstrating that the proton energetically prefers being in the vicinity of the yttrium dopant as in both ‘near’ and
‘planar’ configurations.\textsuperscript{2} This energetic ‘trap’ extends to the 2\textsuperscript{nd} yttrium-oxygen co-ordination shell, as shown by the ground state being the ‘planar’ configuration.

![Graph showing relative energy comparisons](image)

**Figure S10.** Final energies of the four geometrically optimized configurations, relative to the lowest energy configuration (‘planar’) in kJ and eV per mole of protons. The dashed line guides to eye between energetically minimized structures.

A closer inspection of the local environment of the hydroxyl group and dopant presents further distortions. Figure S11 shows this for the two lowest energy configurations; ‘near’ and ‘planar’. A bending of the hydroxyl group towards an oxygen bonded to the yttrium dopant is observed. The closer proximity of O1 and O2 (when M = Y), allows for the formation of stronger hydrogen bonds. Geometric parameters in the vicinity of the proton for all the configurations are given in Table S3. Note that the ‘perpendicular’ and ‘distant’ configurations do not show an appreciable amount of hydrogen bonding.
Figure S11. (a) Schematic of proton local environment. The proton is bonded to oxygen O1 and hydrogen bonded to oxygen O2. O1 and O2 are bonded to the cation centre (M). Local proton geometry from the lowest energy geometrically optimized configurations: (b) ‘near’ and (c) ‘planar’. Zirconium, yttrium, oxygen and hydrogen atoms are in blue, purple, red and white, respectively. Barium atoms have been omitted for clarity.

Table S3. Relative energies, geometrical and GIPAW NMR parameters for all calculated configurations.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Relative energy (kJ mol(^{-1}))</th>
<th>Cation (M)</th>
<th>OH length (Å)</th>
<th>H-bond length (Å)</th>
<th>H-bond angle (°)</th>
<th>Calc. (\delta_{\text{iso}}) ((^1)H) / ppm</th>
<th>Calc. (\delta_{\text{iso}}) ((^{89})Y) / ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near</td>
<td>1.4</td>
<td>Y</td>
<td>0.992</td>
<td>1.99</td>
<td>142</td>
<td>4.5</td>
<td>388</td>
</tr>
<tr>
<td>Planar</td>
<td>0</td>
<td>Zr</td>
<td>1.000</td>
<td>1.80</td>
<td>143</td>
<td>6.8</td>
<td>347</td>
</tr>
<tr>
<td>Perpendicular</td>
<td>20.6</td>
<td>Zr</td>
<td>0.982</td>
<td>2.14</td>
<td>131</td>
<td>2.7</td>
<td>372</td>
</tr>
<tr>
<td>Distant</td>
<td>24.1</td>
<td>Zr</td>
<td>0.985</td>
<td>2.08</td>
<td>131</td>
<td>3.7</td>
<td>400</td>
</tr>
</tbody>
</table>

GIPAW \(^1\)H and \(^{89}\)Y Chemical Shift Calculations

We\(^{10,11,25}\) and others\(^{12,14}\) show that the GIPAW approach to NMR chemical shifts calculations could be predictive, and are used here to assign both \(^1\)H and \(^{89}\)Y NMR spectra of yttrium doped BaZrO\(_3\). \(^1\)H and \(^{89}\)Y chemical shifts for all the configurations have been calculated within the GIPAW approach\(^{22,23}\) and are given in Table S3. It is well known that \(^1\)H chemical shifts can be used to probe the hydrogen bonding in inorganic materials.\(^{26}\) Yesinowski
et al.\textsuperscript{26} demonstrated that \( ^1\text{H} \) isotropic chemical shifts (\( \delta_{\text{iso}} \)) of oxygen-bound hydrogen depended linearly on the O-H…O distance, an index of the hydrogen-bonding strength. The appearance of protons with experimental chemical shifts greater than 5.4 ppm suggests the existence of environments with strong hydrogen bonds.

5. References for supplementary information


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