

Supplemental Information for:

Proton distribution in Sc-doped BaZrO₃: a solid state NMR and First Principle Calculations Analysis

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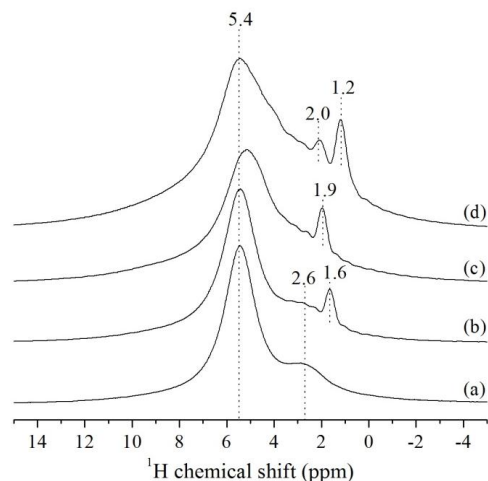
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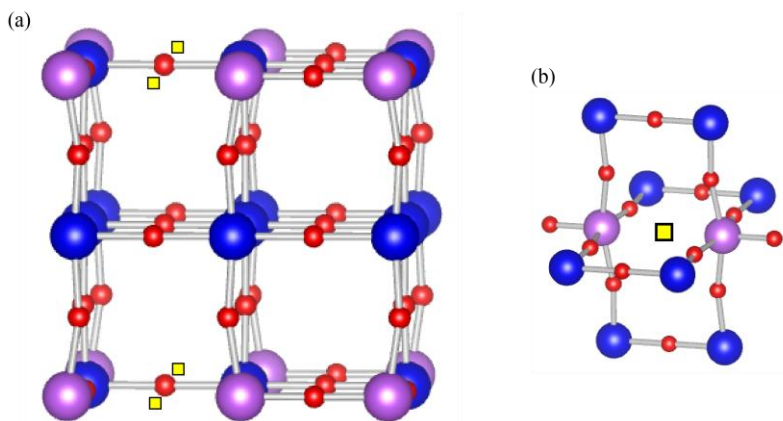
Hydration method

In order to understand the impact of sample preparation and hydration method, we studied the ^1H NMR spectra of two sets of $\text{BaZr}_{0.70}\text{Y}_{0.30}\text{O}_{2.85-y}(\text{OH})_{2y}$ samples. One batch of $\text{BaZr}_{0.70}\text{Y}_{0.30}\text{O}_{2.85-y}(\text{OH})_{2y}$ pellets was prepared by combustion synthesis and then separated into two sets: the first set was crushed manually and the second set was attritor milled at 500 rpm for 4 hours with yttria stabilized zirconia 3 mm balls leading to a higher surface area. Different hydration schemes were then tested on the two sets of powders in order to identify the best hydration method by ^1H NMR. The hand crushed samples were hydrated in a tube furnace. First the powder was dried at 1000°C for 2 h and then cooled down by steps of 100°C every 2 h with wet N_2 flowing over the samples at a rate of $60\text{ mL}\cdot\text{min}^{-1}$. Half of the hand crushed powder was hydrated from 1000°C down to 350°C and the second half from 1000°C down to 200°C . Half of the attritor milled powder was hydrated following the same method, from 1000°C down to 50°C . The second half of the attritor milled sample was hydrated by exposure to ambient atmosphere for several days.

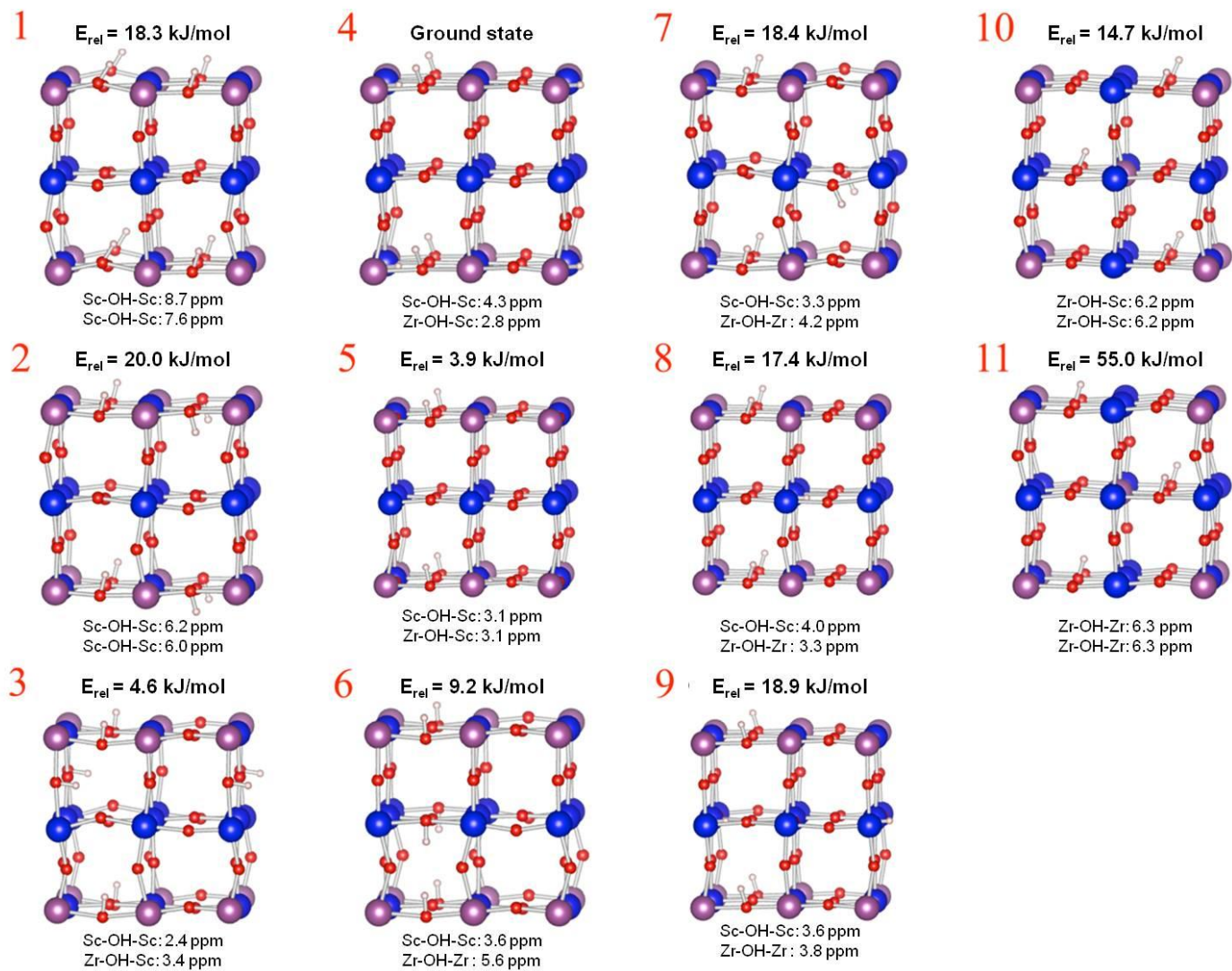
The ^1H NMR spectra of $\text{BaZr}_{0.70}\text{Y}_{0.30}\text{O}_{2.85-y}(\text{OH})_{2y}$ sample resulting from the four different hydration schemes are reported in *Supplemental Figure S1*. The lower the final hydration temperature is, the more resonances are observed. The ^1H NMR spectrum of the hand crushed sample hydrated down to 350°C shows two broad resonances at 5.4 and 2.6 ppm. When the final hydration temperature is lowered down to 200°C , an additional sharper resonance at 1.6 ppm is observed. For the attritor milled samples, the 5.4 ppm resonance is a lot broader than for the previous two hydration schemes and is accompanied by sharper resonances at smaller shifts, at 1.9 ppm for the attritor milled sample hydrated down to 50°C and at both 2 and 1.2 ppm for the sample left under ambient atmosphere. The resonances from 2 to 1.2 ppm, which are sharper, are a signature for mobile protons and likely related to the presence of hydroxide species on the surface of the particles. Due to the higher surface area resulting from mechanical crushing, the attritor milled samples are more subject to the formation of surfacial hydroxide which complicates the NMR spectra. In order to limit their formation while optimizing the hydration level, a final temperature of 200°C was used for hydration of the $\text{BaZr}_{1-x}\text{Sc}_x\text{O}_{3-x}$ samples. A minimum amount of surface species was still detected at 0.6 ppm (Figure 1).



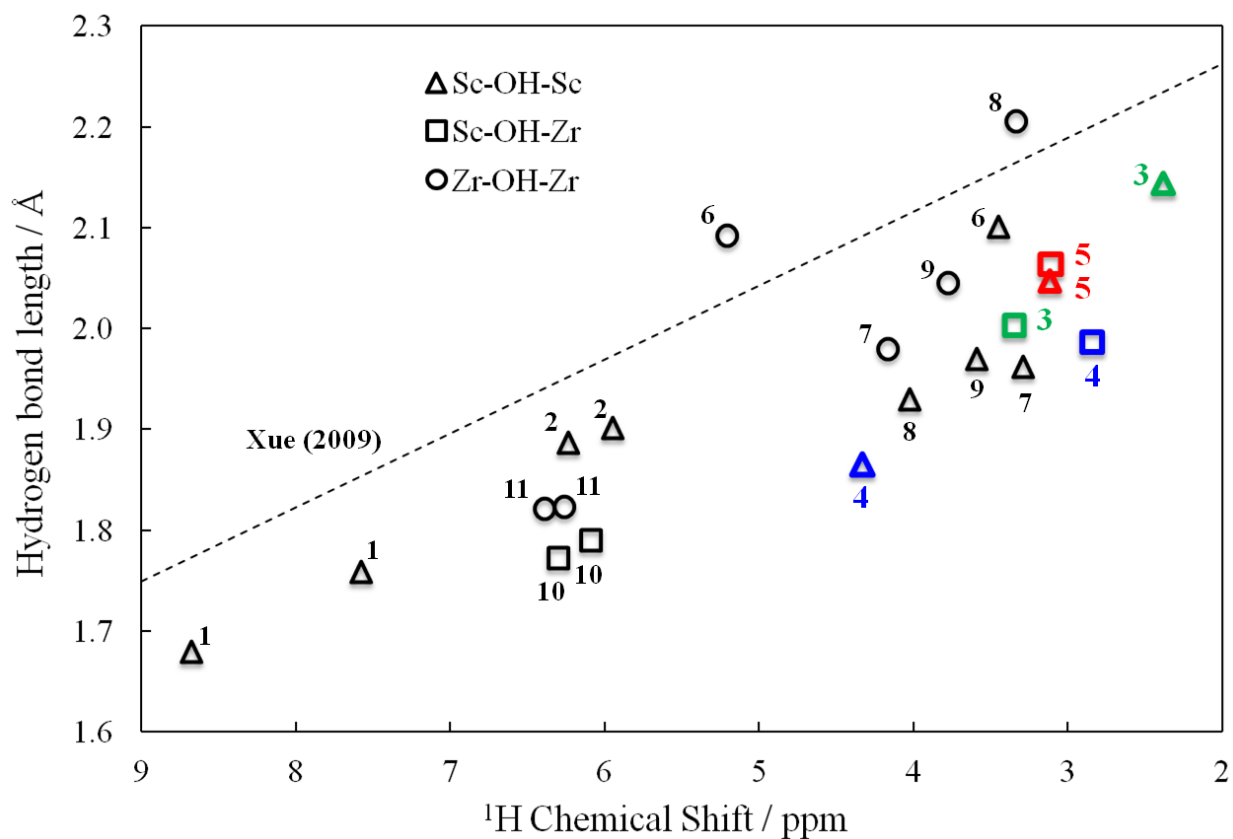
Supplemental Figure S1. ^1H NMR of $\text{BaZr}_{0.70}\text{Y}_{0.30}\text{O}_{2.85-y}(\text{OH})_{2y}$ after different grinding and hydration methods. Hand crushed powders hydrated from 1000°C down to (a) 350°C and (b) 200°C . Attritor milled powders hydrated (c) from 1000°C down to 50°C and (d) by exposure to ambient atmosphere for several days. Spectra referenced to $\text{Si}(\text{CH}_3)_4$.



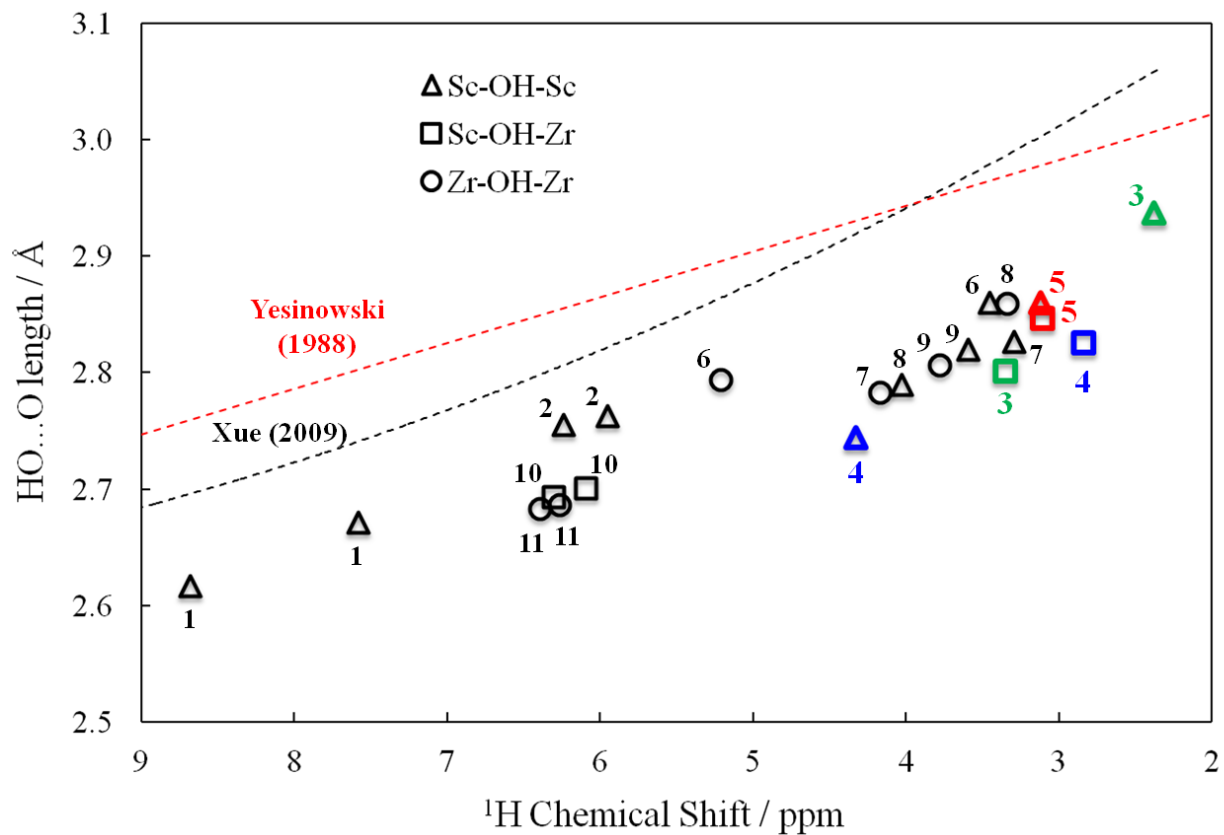
Supplemental Figure S2. Lowest energy structure (a1) for $\text{BaZr}_{0.75}\text{Sc}_{0.25}\text{O}_{2.875}\square_{0.125}$. (a) Tilted view along the c -axis and (b) local geometry around oxygen vacancy showing two 5 co-ordinate scandium atoms. Scandium, zirconium, and oxygen atoms are respectively represented by purple, blue, and red spheres and oxygen vacancies by yellow squares. Barium has been removed for clarity.



Supplemental Figure S3. Ensemble of selected configurations to represent $\text{BaZr}_{0.75}\text{Sc}_{0.25}\text{O}_{2.75}(\text{OH})_{0.25}$ along with their relative energy and calculated ^1H chemical shifts.



Supplemental Figure S4. Calculated ¹H NMR chemical shift versus hydrogen bond length. Proton environments are sorted depending on the metal cation either side of the OH group. The black dotted line represents a line of best fit from experimental NMR and diffraction data collated by Xue.¹



Supplemental Figure S5. Calculated ^1H NMR chemical shifts versus HO...O distance. Dotted lines represent lines of best fit from NMR and diffraction data collated by Xue¹ and Yesinowski.²

References

1. X. Xue and M. Kanzaki, *J. Am. Ceram. Soc.*, 2009, **92**, 2803-2830.
2. J. P. Yesinowski, H. Eckert and G. R. Rossman, *J. Am. Chem. Soc.*, 1988, **110**, 1367-1375.