The role of oxygen vacancies on the vibrational motions of hydride ions in the oxyhydride of barium titanate

(Supplementary Information)

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1 Powder X-ray diffraction

Fig. S1 depicts the PXRD patterns for CA2, CA3 and NAB. Hydride reduction of room temperature tetragonal BaTiO₃ with CaH₂ and NaBH₄ affords a cubic product. The powder patterns of CA2 and CA3 indicated a heterogeneous product, consisting of two cubic phases. The Rietveld plots are shown in Fig. S2 and the result of the Rietveld refinements is compiled in Table S1. A single phase refinement for CA2 and CA3 yielded considerably higher χ^2 values.

2 Thermal gravimetric analysis

TGA should represent a convenient way to assess the H content of $BaTiO_{3-x}H_x$. TGA under flowing air will monitor the reaction $BaTiO_{3-x}H_x + 0.75xO_2 \rightarrow BaTiO_3 + 0.5xH_2O$, according to which a substantial weight increase occurs. The TGA traces of CA2, CA3, and NAB (Fig. S3) show initially a small weight loss (0.1–0.15%) which is attributed to surface water/hydroxyls. The subsequent weight increase, above 200 °C for NAB and 400 °C for CA2 and CA3 should then be due to oxidation according to the chemical equation above. CA2 and CA3 attained weight gains which translates to x = 0.37 and x = 0.19, respectively (*cf.* Tab. 1). The corresponding value for NAB is very high (x = 0.75) and actually exceeds considerably the considered maximum value for stable BaTiO_{3-x}H_x ($x \approx 0.6$).

3 Nuclear magnetic resonance analysis

The ¹H MAS NMR spectra are shown in Fig. S4. The precursor material, tetragonal BaTiO₃, displays distinct resonances at 1.1, 4.8 and 6.5 ppm which are attributed to surface OH species and water because the spectrum after heating this material to 900 °C, which would remove any structural OH, is virtually identical. When quantifying the H content of the BaTiO₃ precursor by relating its ¹H NMR signal intensity to that of adamantane ($C_{10}H_{16}$) in the same rotor volume and under identical conditions, one obtains a molar ratio H:BaTiO₃ \approx 0.039. (The density and molecular weight of adamantane is 1.08 g/cm³ and 136.23 g/mol; the density and molecular weight of BaTiO₃ is 6.02 g/cm³ and 233.2 g/mol.)

The spectra of NAB, CA3, and CA2 show a broad resonance at around -4, -15, and -20 ppm, respectively. This is distinct from the precursor and the signal is attributed to hydridic H on the O position in the perovskite structure. In addition, there are sharp resonances in the positive 1–7 ppm region, similar to the precursor spectrum, which are, thus, surface OH species. The concentration of protic surface hydroxyl is comparable for the precursor and the reduced samples. One can estimate the molar ratio between hydridic H and BaTiO₃ in the reduced samples to be approximately 0.04, 0.12, and 0.08, respectively (see Table 1). The large discrepancy with the TGA experiments (*cf.* Fig. S3), delivering *x* values of 0.75, 0.19, and 0.37 with respect to BaTiO_{3-*x*}H_{*x*}, respectively, has to be attributed to a simultaneous presence of O vacancies (\Box). Thus we reformulated the composition of the reduced BaTiO₃ samples as BaTiO_{3-*x*}H_{*y*} \Box_{x-y} . The *x* and *y* values are given in Table 1.



Fig. S1 PXRD patterns (Cu K a radiation) for CA2, CA3, and NAB. The PXRD pattern of BaTiO3 is included for comparison.



Fig. S2 Rietveld fit to the PXRD data of the CA2, CA3, and NAB samples. The corresponding fit parameters are shown in Table S1.

Table S1 Summary of Rietveld refinement results for CA2, CA3, and NAB. Numbers between square parenthesis indicate the phase fraction when two phases were used in the refinement.

Sample ID		Lattice parameter (Å)	Cell volume (Å ³)	χ^2	<i>R</i> _{Bragg}	R _F
CA3	(single phase refinement)	4.0080(1)	64.38(1)	1.64	2.90	1.63
CA3	(two phase refinement)	Phase 1: 4.0075 [88(1)%]	64.36(1)	0.957	2.74	1.48
		Phase 2: 4.0183(2) [12%]				
CA2	(single phase refinement)	4.0147(2)	64.71(1)	1.72	3.43	2.28
CA2	(two phase refinement)	Phase 1: 4.0119(1) [79(1)%]	64.580(5)	0.841	2.70	1.97
		Phase 2: 4.0295(1) [21%]				
NAB		4.0044(1)	64.210(1)	0.880	2.09	1.69



Fig. S3 TGA traces for CA2, CA3, and NAB samples.



Fig. S4 ¹H MAS NMR spectra of the precursor material tetragonal BaTiO₃ and the reduced samples (a) CA2 and CA3 collected at the magnetic field of 9.4 T, and (b) NAB acquired at the magnetic field of 14.1 T. The inset in each panel shows proton signal intensity with respect to BaTiO₃.

4 Inelastic neutron scattering measurements on BaTiO₃

Fig. S5 shows the INS spectrum as recorded on a pure $BaTiO_3$ sample at T<10 K on TOSCA. The spectrum of CA3, measured in the same experimental conditions, is shown for comparison. Above 100 meV, the spectrum of $BaTiO_3$ is essentially flat, whereas the spectrum of CA3 is characterized by intense features assigned to the (local) vibrational dynamics of the hydride ions. Below 100 meV (inset) the spectra of $BaTiO_3$ and CA3 are characterized by weak bands assigned to the lattice vibrations. We remark that $BaTiO_3$ is characterized by a rhombohedral structural arrangement at low temperatures, whereas in the oxydride phase the structural arrangement is cubic.

5 Calculated weighted vibrational density of states

Fig. S6 (a-b) show the calculated weighted vibrational density of states for pristine BaTiO₃ and BaTiO₃ containing one oxygen vacancy (v_O^{\times}) , respectively. Fig. S6 (c-f) show the weighed vibrational density of states calculated for BaTiO_{3-x}H_y in the presence of (c-d) a hydride ion on a oxygen site (H_O^{\times}) and (e-f) a hydride ion on an oxygen site and an oxygen vacancy as second nearest neighbour $(H_Ov_O^{\times})$. Each configuration was first calculated in a 2 × 2 × 2 supercell, corresponding to an oxyhydride ion concentration of *y* = 0.125, and then in a 3 × 3 × 3 supercell, corresponding to an oxyhydride ion concentration of *y* = 0.037.

For both pristine BaTiO₃ and BaTiO₃ containing one oxygen vacancy the only visible spectral contributions are located below 100 meV [Fig. S6 (a-b)]. This region can be therefore assigned to the lattice vibrations of the perovskite structure.



Fig. S5 INS spectra at T < 10 K of BaTiO₃ and CA3 as recorded on TOSCA. The inset shows a zoom in the low energy region.

Note that the intensity in the region below 100 meV is very low, and spectra below the dashed line (at 100 meV) are therefore amplified by a factor 25 for visibility. We remark that, according to the results in Fig. S6, the introduction of oxygen vacancies and hydride ions does not affect significantly the lattice vibrational modes of the perovskite structure, even though small differences can be observed.

Peaks in the region above 100 meV can be observed only when introducing a hydride ion in the structure, see Fig. S6 (c-f). The fact that these peaks are more intense in the calculation for the $2 \times 2 \times 2$ supercell, with respect to the $3 \times 3 \times 3$ supercell, is simply a consequence of the lower hydrogen concentration in the latter.

Concerning the size of the supercell, we can observe only minor shifts of peaks above 100 meV between the calculations for different supercell sizes. This confirms that a $2 \times 2 \times 2$ supercell is sufficiently large to capture the vibrational properties of the system under investigation. Further, the data suggest that the vibrational frequencies calculated for the hydride ion are only weakly dependent on the hydrogen concentration.

The weighted vibrational density of states is closely related to the INS intensity (see also ref. S1). It is computed as

$$S(\boldsymbol{\omega}) = \sum_{\mathbf{v}} \sigma_{\mathbf{v}} \frac{m_n}{m_v} g_{\mathbf{v}}(\boldsymbol{\omega}) \exp\left[-\frac{2m_n \boldsymbol{\omega}}{3\hbar} \langle u_{\mathbf{v}}^2 \rangle\right],\tag{1}$$

where σ_V and m_V are the total neutron scattering cross section and atomic mass of the vth atom, m_n is the neutron mass and $\langle u_V^2 \rangle$ is the atomic mean square displacement evaluated at T = 0 K. The exponential factor is the Debye-Waller factor and

$$g_{\nu}(\omega) = \frac{1}{N} \sum_{\mathbf{q}j} |\mathbf{e}_{\mathbf{q}j}^{\nu}|^2 \,\delta(\omega - \omega_{\mathbf{q}j})$$
⁽²⁾

is the partial phonon density of states, where *N* is the number of unit cells, ω_{qj} is the eigenfrequency for phonon mode *j* with wavevector **q** and \mathbf{e}_{qj}^{v} is the corresponding eigenvector projected onto atomic species *v*.^{S2} For the total neutron scattering cross sections σ_v of H, Ba, Ti, and O we use 82.0, 3.38, 4.35, and 4.23 barn, respectively.^{S3}

Fig. S7 completes the study by showing the weighted density of states for $BaTiO_3$ containing (a) one hydrogen on one oxygen site and one oxygen vacancy ($H_0v_0^{\times}$), (b) two hydrogens on two oxygen sites and two oxygen vacancies ($2 \times H_0v_0^{\times}$), and (c) three hydrogens on three oxygen sites and three oxygen vacancies ($3 \times H_0v_0^{\times}$), computed in a $3 \times 2 \times 3$ supercell.



Fig. S6 (a-b) Weighted density of states for (a) pristine BaTiO₃ and (b) BaTiO₃ containing one oxygen vacancy, v_0^{\times} . (c-d) Weighted density of states for BaTiO₃ containing one hydrogen on an oxygen site (H_0^{\times}), computed in a 2 × 2 × 2 (c) and in a 3 × 3 × 3 (d) supercell. (e-f) Weighted density of states for BaTiO₃ containing one hydrogen on an oxygen site and an oxygen vacancy ($H_0v_0^{\times}$), computed in a 2 × 2 × 2 (e) and in a 3 × 3 × 3 (f) supercell. We have used a Gaussian smearing of 0.5 meV to compensate for the finite *k*-point sampling. The spectra below the dashed line at 100 meV are amplified by a factor of 25.



Fig. S7 Weighted density of states for BaTiO₃ containing (a) one hydrogen on one oxygen site and one oxygen vacancy ($H_Ov_O^{\times}$), (b) two hydrogens on two oxygen sites and two oxygen vacancies ($2 \times H_Ov_O^{\times}$), and (c) three hydrogens on three oxygen sites and three oxygen vacancies ($3 \times H_Ov_O^{\times}$), computed in a $3 \times 3 \times 3$ supercell. We have used a Gaussian smearing of 0.5 meV for frequencies below 100 meV to compensate for the finite *k*-point sampling ($6 \times 6 \times 6$ in the $3 \times 3 \times 3$ cell). We have, however, used a smearing of only 0.1 meV for frequencies above 100 meV in order not to obscure the highly localised nature of the hydrogen vibrational modes The spectra below the dashed line at 100 meV are amplified by a factor of 50.

6 Variable temperature inelastic neutron scattering measurements

Fig. S8 shows the INS spectra of CA2, as measured on MERLIN at 7 K, 240 K, and 280 K, respectively. There are no large differences between the spectra measured at the three different temperatures.



Fig. S8 Variable temperature INS spectra of CA2 as recorded on MERLIN.

References

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