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Supplementary Materials

Barium Titanium Oxynitride from Ammonia-Free Nitridation of Reduced $BaTiO_3$

Hua Guo [1], Aleksander Jaworski [1], Zheng Chen [2], Can Lu [2], Adam Slabon [1] and Ulrich Häussermann [1,*]

[1] Department of Materials and Environmental Chemistry, Stockholm University, SE-10691 Stockholm, Sweden; hua.guo@mmk.su.se (H.G.); aleksander.jaworski@mmk.su.se (A.J.); adam.slabon@mmk.su.se (A.S.)

[2] Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, DE-52074 Aachen, Germany; zheng.chen@ac.rwth-aachen.de (Z.C.); can.lu@ac.rwth-aachen.de (C.L.)

* Correspondence: ulrich.haussermann@mmk.su.se; Tel.: +46-08-162390

PXRD analysis of BTOH

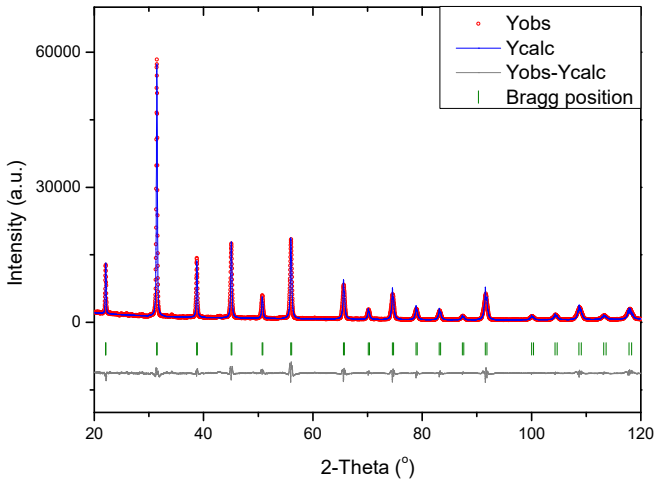

Figure S1. Rietveld fit to the PXRD data of the oxyhydride starting material $BaTiO_{2.60}H_{0.08}\square_{0.32}$ (BTOH).

Sample	Unit cell parameters (Å)	Unit cell volume (Å^3)	χ^2	R_{Bragg}	R_F
BTOH	4.0220 (2)	65.062 (1)	9.86	4.42	2.73

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^{1}H-MAS NMR analysis of BTOH

^{1}H MAS NMR has been used earlier for the analysis of metal hydride reduced $BaTiO_3$ samples[1]. ^{1}H MAS NMR is especially useful for unambiguously determining the hydridic H content, which then allows the deduction of O defect concentrations from TGA measurements. Importantly, protonic H from (surface) hydroxyl and hydridic H as part of the bulk structure can be discriminated as positive and negative chemical shift contributions, respectively, in the spectra. Hydridic H typically expresses itself as a single broad resonance peak at negative chemical shift whereas protonic resonances at ~1 ppm and in the region 6 – 7 ppm correspond to surface OH species and secondary water, respectively. The amount of hydridic H in reduced samples can be quantified by relating the ^{1}H NMR signal of the $BaTiO_3$ starting material to that of adamantane ($C_{10}H_{16}$) in the same rotor volume and under identical experimental conditions. From the density and molecular weights of adamantane (1.08g/cm^3, 136.23 g/mol) and $BaTiO_3$ (6.02 g/cm^3, 233.2 g/mol) a molar ratio H/$BaTiO_3$ can be established for reduced samples. With the knowledge of the hydridic H concentration, the corresponding weight increase for $BaTiO_{3-x}H_x + 0.75x\ O_2 \rightarrow BaTiO_3 + 0.5x\ H_2O$ can be calculated. The difference to the actual weight increase in the TG experiment is then attributed to the simultaneous presence of O vacancies, $x_{\square}$, see Table 1.

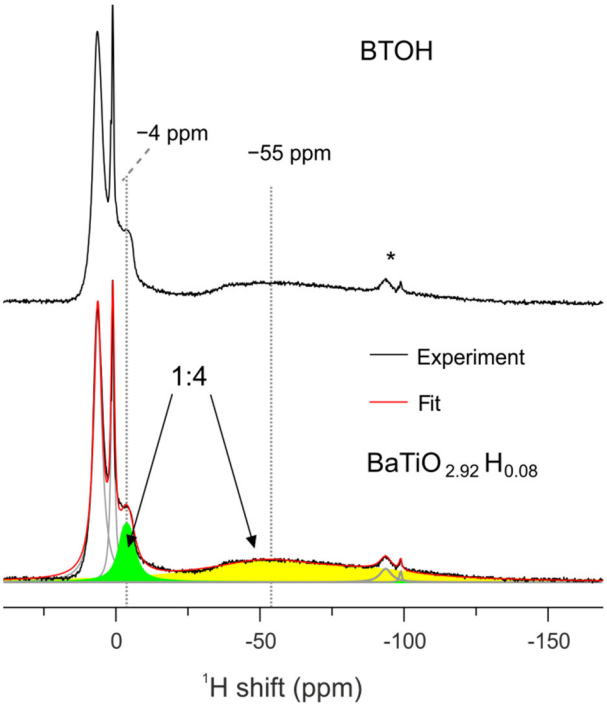

Figure S2: ^{1}H MAS NMR spectrum of BTOH. The proton signal is deconvoluted into a protonic (positive parts per million) and hydridic (negative parts per million) part [1]. The hydridic contribution in turn constitutes two contributions, one centered at -4 ppm and one at -55 pm, with a ratio of 1:4 (according to the integrated proton signal intensity). The occurrence of two hydridic environments in reduced $BaTiO_3$ is highly unusual and perhaps relates to the large O defect concentration of BTOH. Previously sharp signals with small negative shifts have been observed in reduced samples with high defect concentration (e.g. when using $NaBH_4$ as reducing agent [1]). One may speculate that the two H^- environments in BTOH are associated with a different number and/or different arrangement of O defects around H^-.

Additional TG/DSC analysis

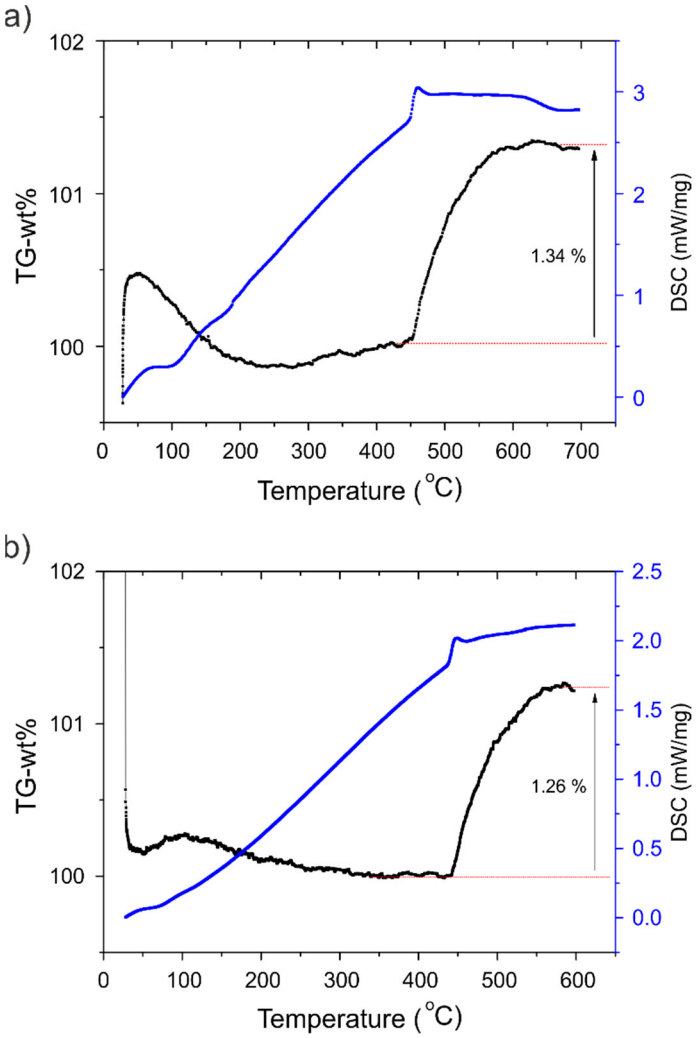

Figure S3. Simultaneously measured TG and DSC traces for BTOH upon heating under a dry N_2 stream up to 700 °C with heating rate 10 °C/min (a) and to 600 °C with a heating rate 5 °C/min (b).

PXRD analysis of BTON

Table S1. Refinement result summary for BTON samples using the tetragonal structure model

Sample	Unit cell parameters (Å)	Unit cell volume (Å^3)	χ^2	R_{Bragg}	R_F
BTON-500-0h	a= 4.0121 (2) c= 4.0177 (3)	64.672 (2)	4.59	4.45	3.30
BTON-500-2h	a= 4.0074 (4) c= 4.0202 (6)	64.562 (3)	4.30	6.09	4.48
BTON-600-0h	a= 4.0103 (7) c= 4.0192 (11)	64.639 (6)	3.79	8.89	7.34
BTON-600-2h	a= 4.0086 (3) c= 4.0180 (5)	64.565 (3)	4.32	5.34	3.62
BTON-600-6h	a= 4.0085 (3) c= 4.0184 (2)	64.568 (2)	4.25	5.45	3.66

Table S2. Refinement result summary for BTON samples using the cubic structure model

Sample	Unit cell parameters (Å)	Unit cell volume (Å^3)	χ^2	R_{Bragg}	R_F
BTON-500-0h	4.0137 (1)	64.659 (1)	3.96	3.68	2.70
BTON-500-2h	4.0119 (2)	64.575 (1)	4.87	5.25	4.20
BTON-600-0h	4.0131 (3)	64.630 (2)	3.71	7.10	5.86
BTON-600-2h	4.0118 (3)	64.569 (2)	5.07	4.90	3.52
BTON-600-6h	4.0111 (2)	64.533 (2)	4.90	4.71	3.25

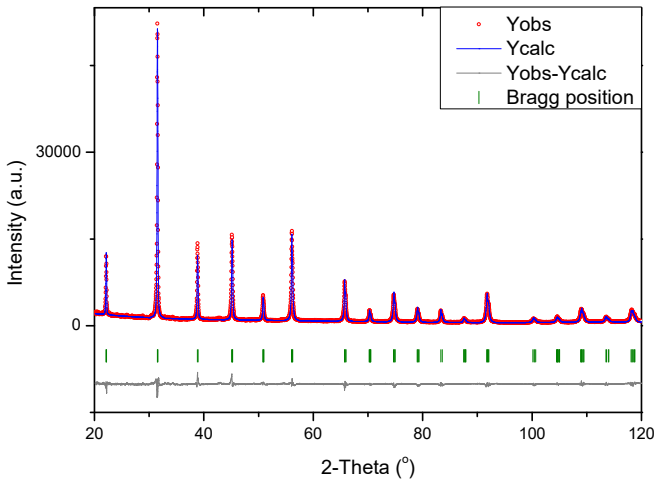

Figure S4. Refinement of BTON-500C-0h as tetragonal phase.

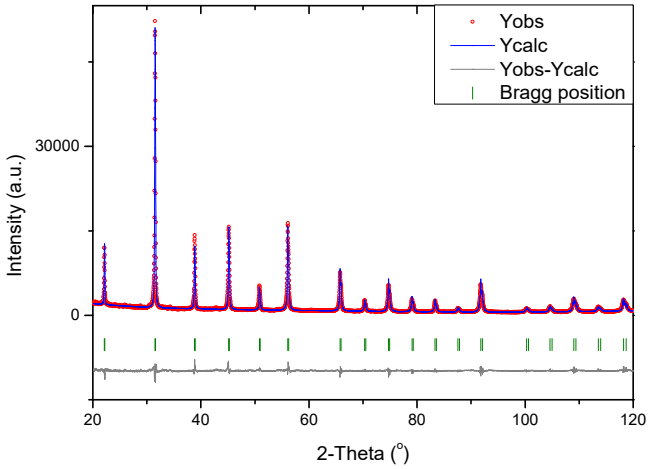

Figure S5. Refinement of BTON-500C-0h as cubic phase.

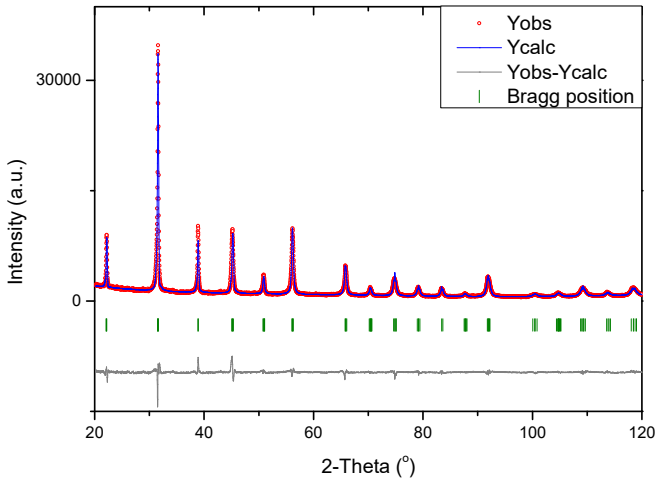

Figure S6. Refinement of BTON-500C-2h as tetragonal phase.

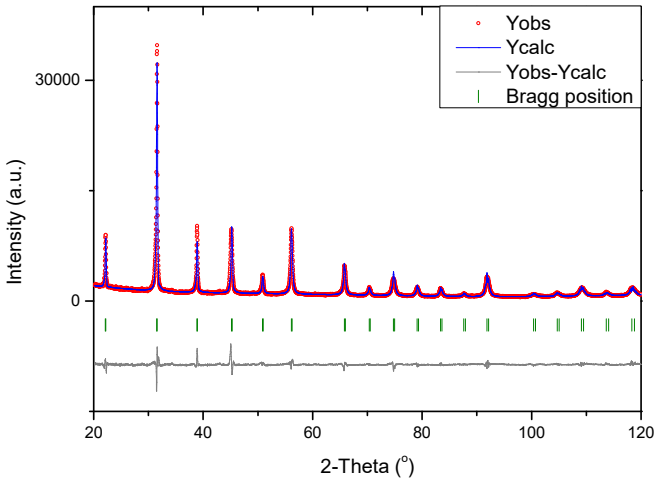

Figure S7. Refinement of BTON-500C-2h as cubic phase.

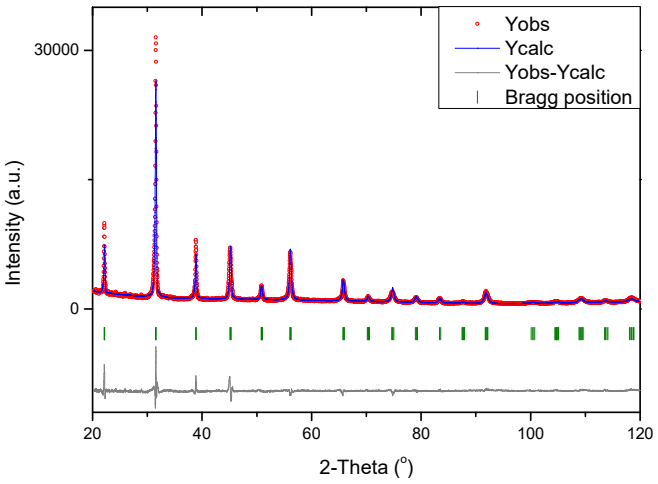

Figure S8. Refinement of BTON-600C-0h as tetragonal phase.

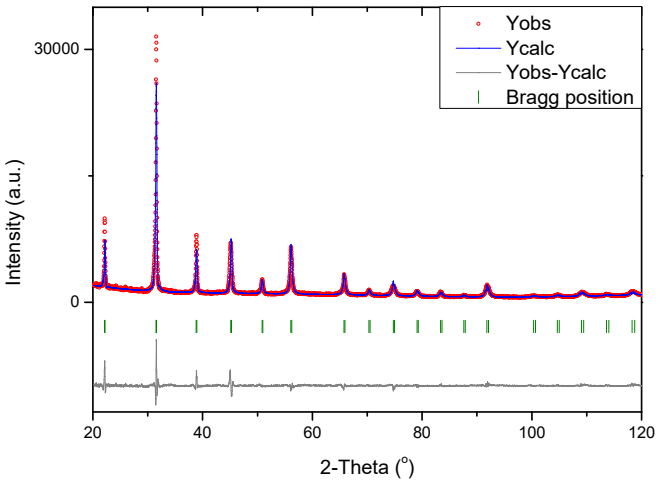

Figure S9. Refinement of BTON-600C-0h as cubic phase.

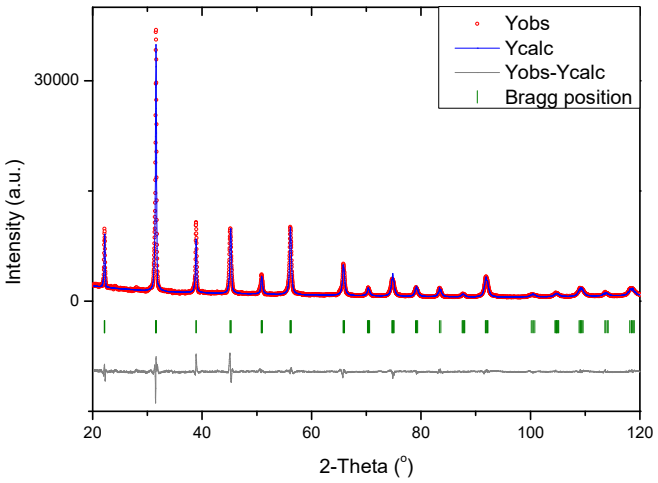

Figure S10. Refinement of BTON-600C-2h as tetragonal phase.

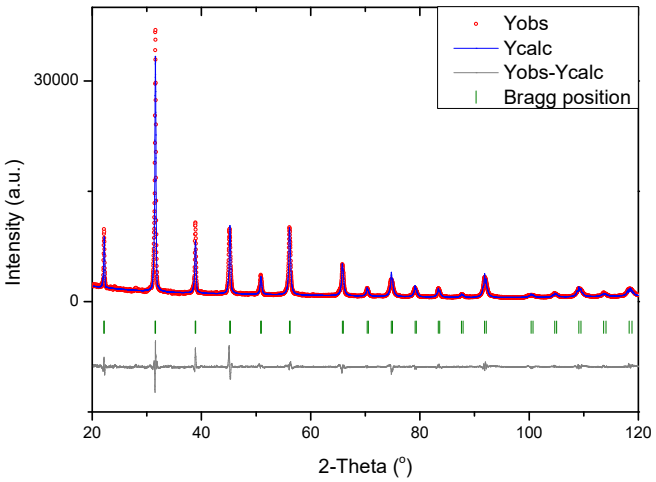

Figure S11. Refinement of BTON-600C-2h as cubic phase.

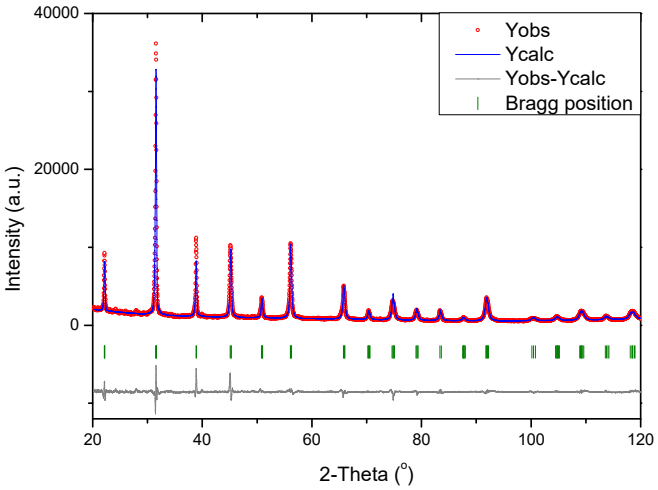

Figure S12. Refinement of BTON-600C-6h as tetragonal phase.

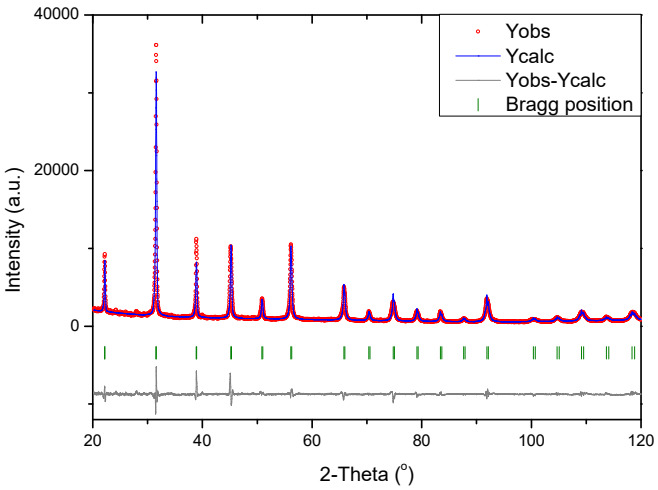

Figure S13. Refinement of BTON-600C-6h as cubic phase.

Band gap analysis

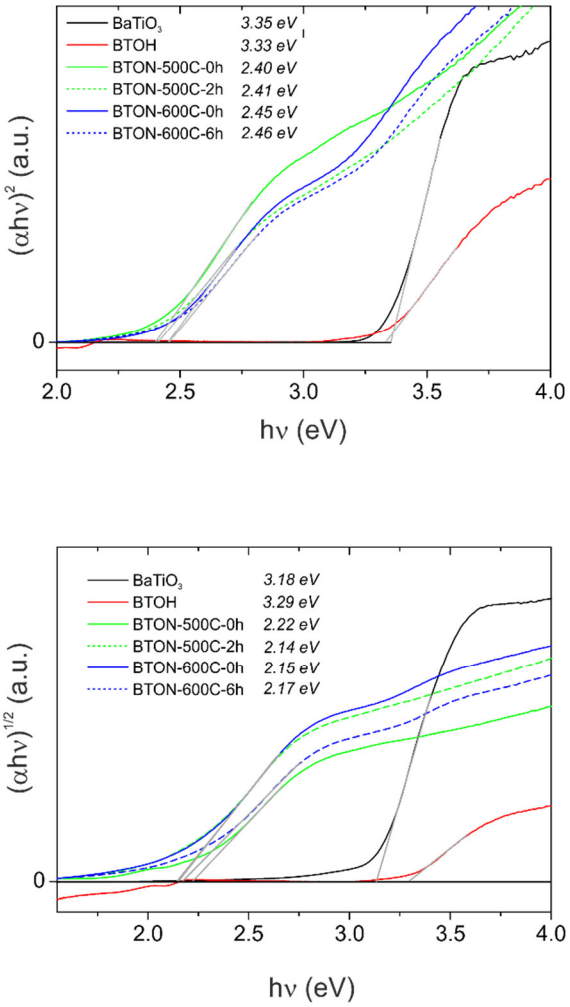

Figure S14. Tauc plots for direct (upper figure) and indirect (lower figure) band gap evaluation of $BaTiO_3$, BTOH, BTON-500C-0h, BTON-500C-2h, BTON-600C-0h, and BTON-600C-6h.

References

1. Nedumkandathil, R.; Jaworski, A.; Grins, J.; Bernin, D.; Karlsson, M.; Eklof-Osterberg, C.; Neagu, A.; Tai, C.-W.; Pell, A.J.; Haussermann, U. Hydride Reduction of $BaTiO_3$ - Oxyhydride Versus O Vacancy Formation. *ACS OMEGA* **2018**, *3*, 11426–11438, doi:10.1021/acsomega.8b01368.