Potassium Octahydridotriborate: Diverse Polymorphism in a Potential Hydrogen Storage Material and Potassium Ion Conductor

Supplementary Information

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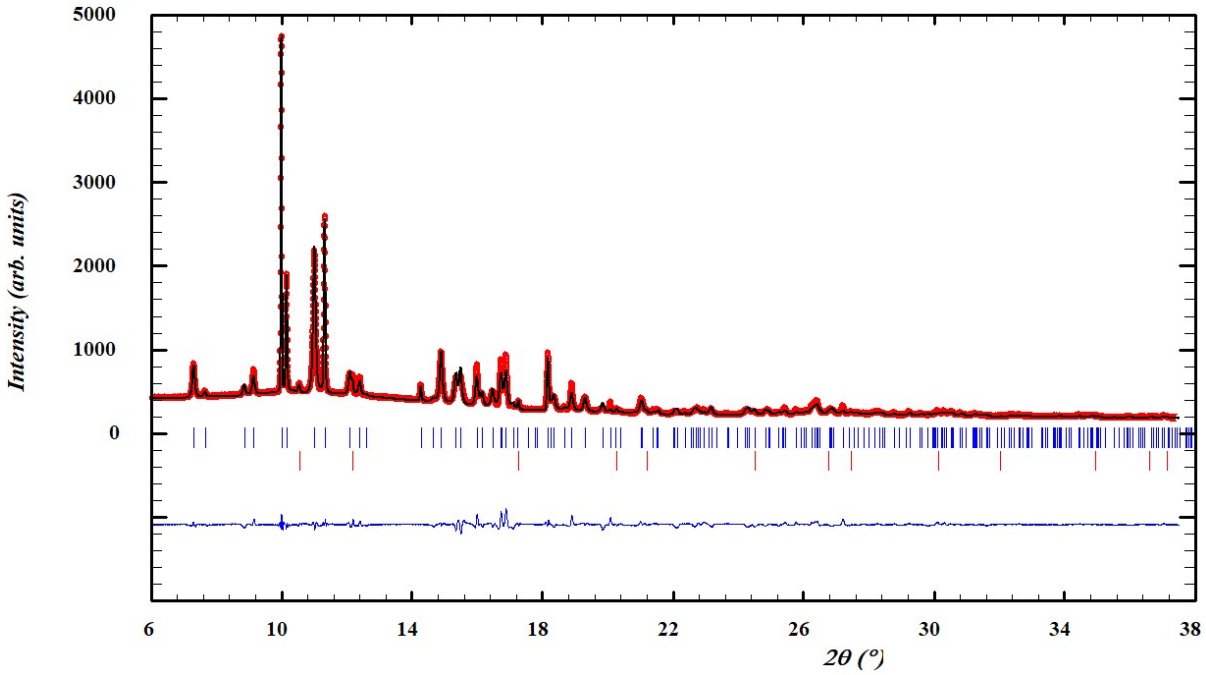

Figure S1. Rietveld refinement plot of SR PXD data measured at −52 °C, λ = 0.70848 Å, for α-KB_3H_8, showing experimental (red circles) and calculated (black line) PXD patterns, and a difference plot below (blue line). Top tick (α-KB_3H_8, $P2_1/m$, 98.9 wt%), bottom tick (KBH_4, *Fm-3m*, 1.1 wt%). Final discrepancy factors: R_p = 2.51 %, R_{wp} = 4.02 % (not corrected for background), R_p = 14.6 %, R_{wp} = 18.6 % (conventional Rietveld R-factors), $R_{Bragg}(KB_3H_8)$ = 6.26 %, $R_{Bragg}(KBH_4)$ = 7.86 %, and global χ^2 = 27.9. Due to anisotropic peak broadening, selected *hkl* reflections (*-111, -101, -121, -131, 020*) were refined as described in reference [1]

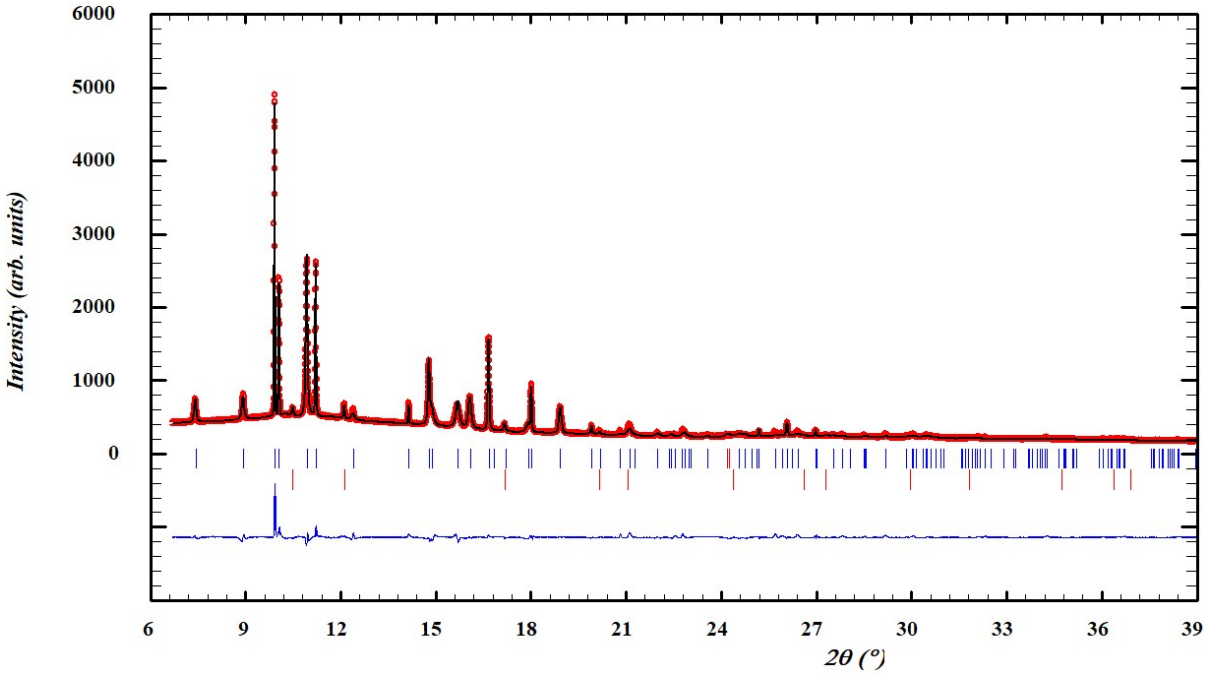

Figure S2. Rietveld refinement plot of SR PXD data measured at 25 °C, λ = 0.70848 Å, for α′-KB_3H_8, showing experimental (red circles) and calculated (black line) PXD patterns, and a difference plot below (blue line). Top tick (α'-KB_3H_8, *Cmcm*, 98.5 wt%), bottom tick (KBH_4, *Fm-3m*, 1.5 wt%). Final discrepancy factors: R_p = 2.12 %, R_{wp} = 2.74 % (not corrected for background), R_p = 16.4%, R_{wp} = 15.4 % (conventional Rietveld R-factors), R_{Bragg}(α'-KBH_4) = 7.82 %, R_{Bragg}(KBH_4) = 13.8 %, and global χ^2 = 46.2. Due to anisotropic peak broadening, selected *hkl* reflections (*021, 020, 002, 022, 202, 113, 023, 043, 115, 025, 004, 200, 130, 132*) were refined as described in reference [1]

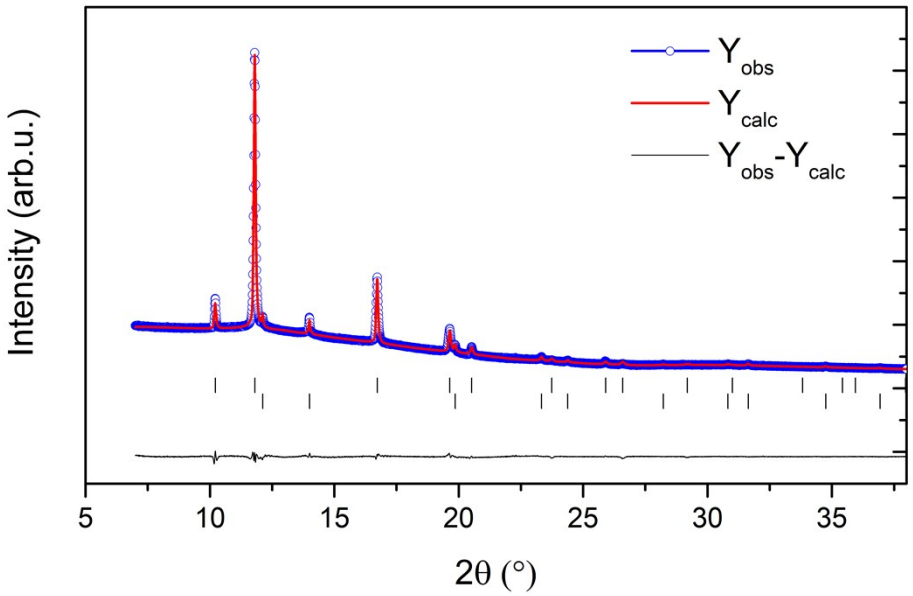

Figure S3. Rietveld refinement plot of SR PXD data measured at 50 °C, λ = 0.824598 Å, for β-KB_3H_8, showing experimental (blue circles) and calculated (red line) SR PXD patterns, and a difference plot below (dark grey). Top tick (β-KB_3H_8, *Fm-3m*), bottom tick (KBH_4, *Fm-3m*). Final discrepancy factors: R_p = 1.00 %, R_{wp} = 1.45 % (not corrected for background), R_p = 18.7 %, R_{wp} = 9.37 % (conventional Rietveld R-factors), R_{Bragg}(β-KB_3H_8) = 4.21 %, R_{Bragg}(KBH_4) = 16.5 %, and global χ^2 = 6.12.

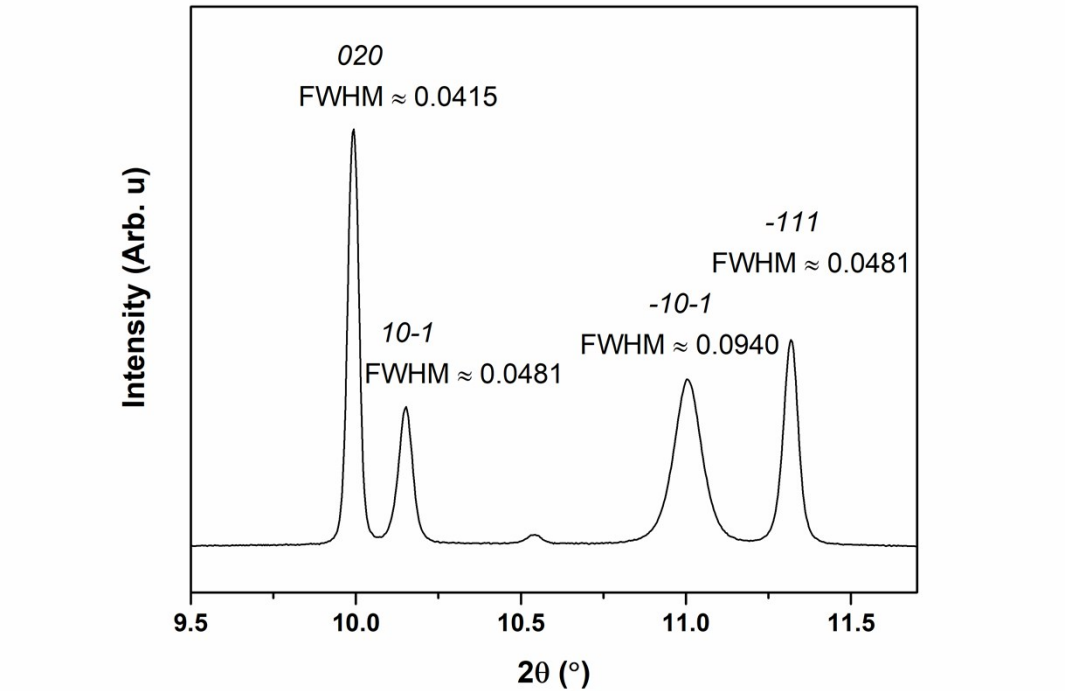

Figure S4. SR PXD data measured at –52 °C, λ = 0.70848 Å, for α-KB_3H_8, shown in the 2θ range 9.5 to 11.7°. The full width half maximum values are provided for four selected *hkl* reflections.

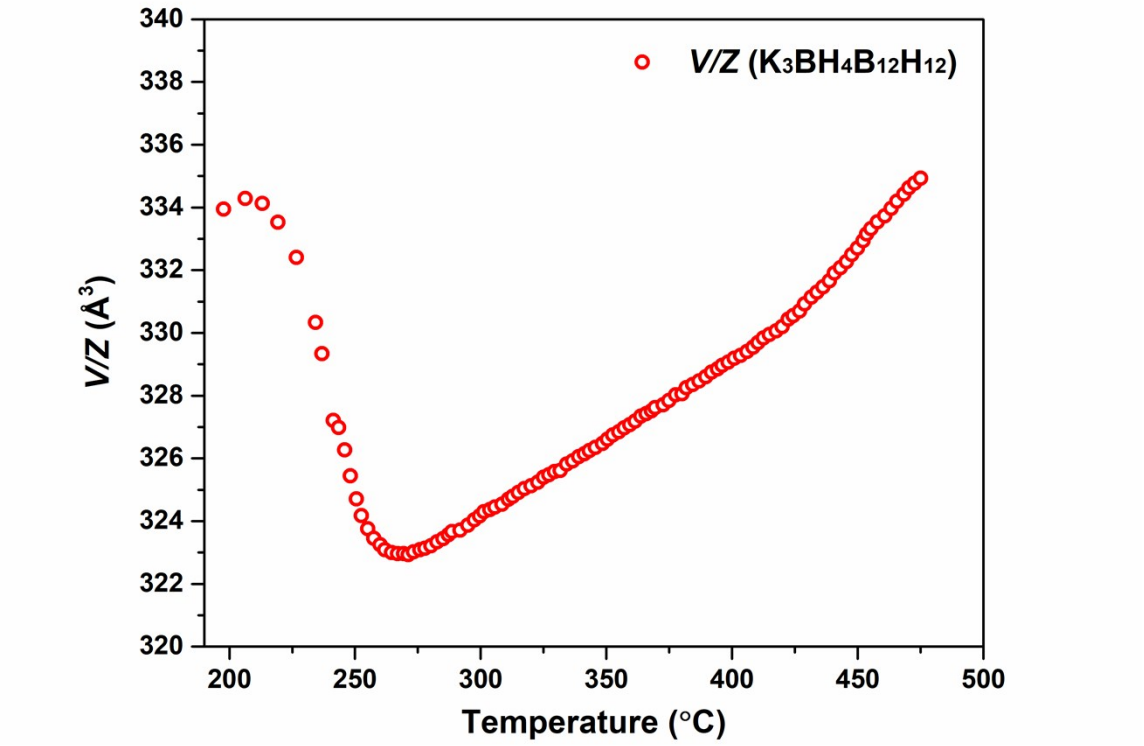

Figure S5: Volume per formula unit (*V/Z*) extracted from sequential Rietveld refinement of $K_3BH_4B_{12}H_{12}$ from SR PXD data of the as synthesized KB_3H_8 sample measured at Diamond (λ = 0.824598 Å) in the temperature range 198 to 475 °C.

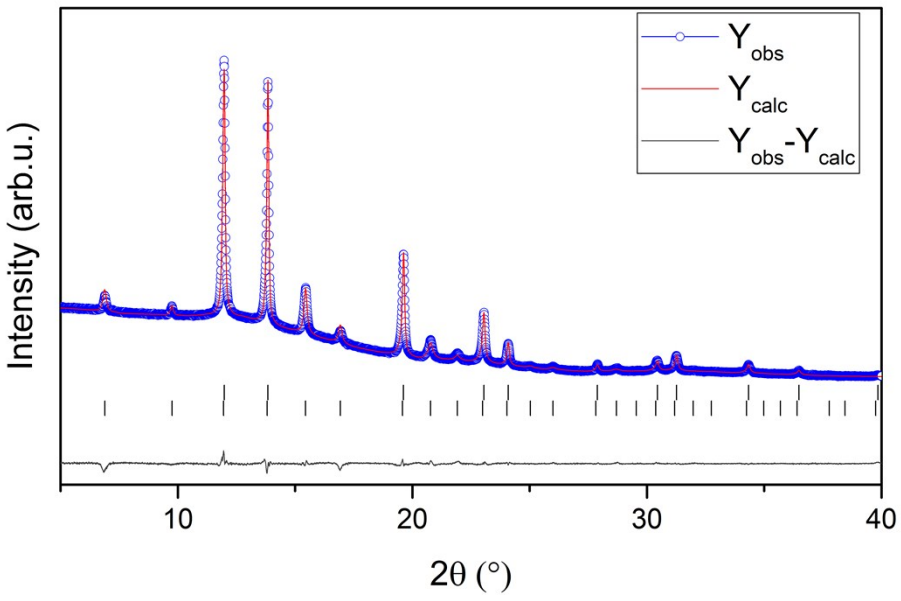

Figure S6. Rietveld refinement plot of SR PXD data measured at 253 °C, λ = 0.824958 Å, for KB_3H_8, showing experimental (blue circles) and calculated (red line) SR PXD patterns, and a difference plot below (dark grey). Top tick (KBH_4, *Fm*-3*m*, 21.7 wt%), bottom tick ($K_3BH_4B_{12}H_{12}$, *Pm*-3, 78.3 wt%). Final discrepancy factors: R_p = 0.45 %, R_{wp} = 0.90 % (not corrected for background), R_p = 5.52 %, R_{wp} = 11.13 % (conventional Rietveld R-factors), $R_{Bragg}(KBH_4)$ = 1.19 %, $R_{Bragg}(K_3BH_4B_{12}H_{12})$ = 2.18 %, and global χ^2 = 5.75.

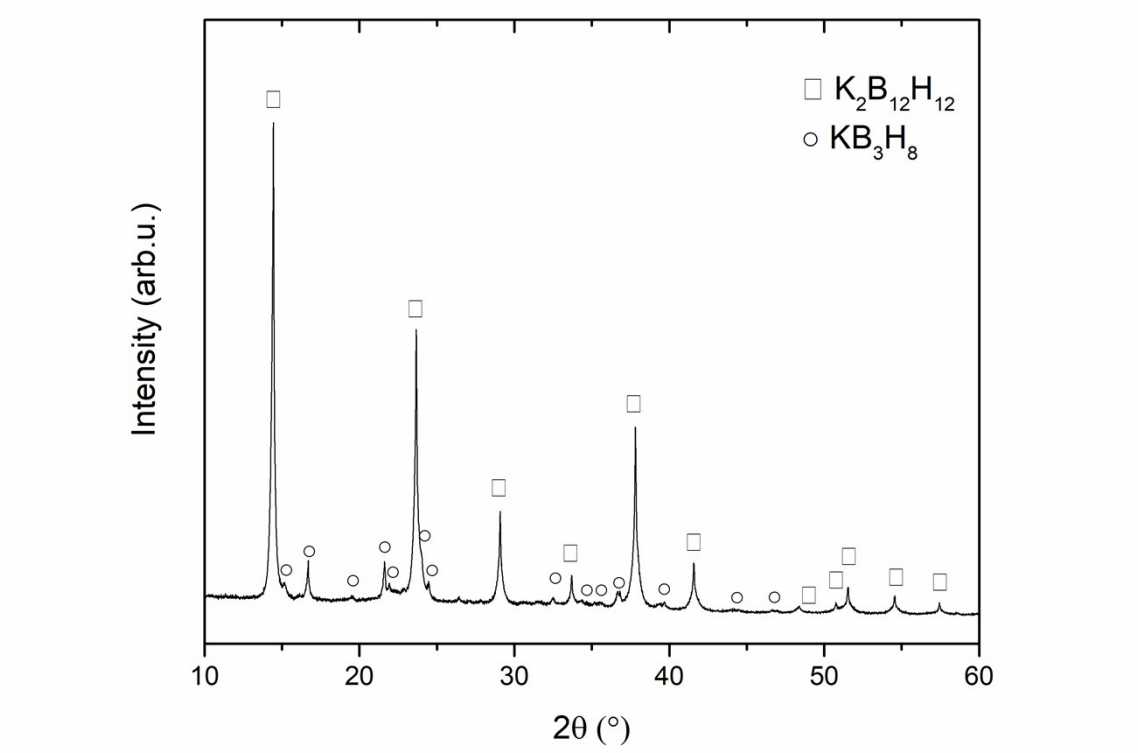

Figure S7. PXD pattern of sample **s5** measured at *RT*, λ = 1.54056 Å. Two crystalline compounds, $K_2B_{12}H_{12}$ and KB_3H_8, are observed.

References

1. J. Rodríguez-Carvajal. Study of Micro-Structural Effects by Powder Diffraction Using the Program FULLPROF. Available at: http://www.cdifx.univ-rennes1.fr/fps/Microstructural_effects.pdf (accessed 09-04-2019)