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Solid state synthesis, structural characterization and ionic conductivity of bimetallic alkali-metal yttrium borohydrides $MY(BH_4)_4$ (M = Li and Na)

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SUPPORTING INFORMATION

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- **Figure S10 -** High resolution PXD and refinement of $NaY(BH_4)_4$, space group *Cmcm*
- **Figure S11 -** High resolution PXD and refinement of $NaY(BH_4)_4$, space group $C222_1$

1.

Table S1 - Optimized unit cell parameters and energy with respect to the most stable Li@2*a* structure.

	a (Å)	*c* (Å)	Energy (eV/f.u.)
Exp.	6.236	12.491	
2*a*	6.222	12.486	0.000 (reference)
2*b*	6.461	12.538	0.348
2*d*	6.464	12.539	0.348
2*e*	6.338	12.617	0.412
2*f*	6.332	12.954	0.350
I-4	6.553	12.476	-0.185

Table S2 - Experimental and DFT-optimized cell parameters and unit cell volume per formula unit (*V*/*Z*).

		a / Å	*b* / Å	*c* / Å	*V*/*z* / Å^3
Exp		8.5260	12.1358	9.0526	234.2
Cmcm	PBE	8.506	12.415	9.334	246.4
	vdW-DF2	8.494	12.166	8.866	229.1
$C222_1$	PBE	9.819	12.149	9.730	290.2
	vdW-DF2	8.516	12.134	8.881	229.5

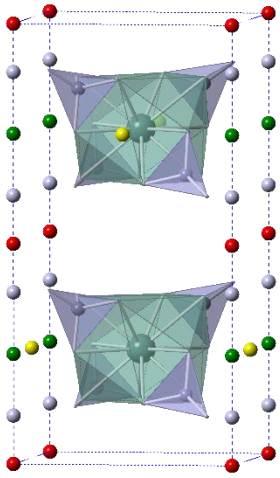

Figure S1 - Crystal structure of $LiY(BH_4)_4$, showing the considered Li positions: 2*a* in green, 2*b* in yellow, 2*e* in red, 4*k* in pale violet.

(a) (b) (c)

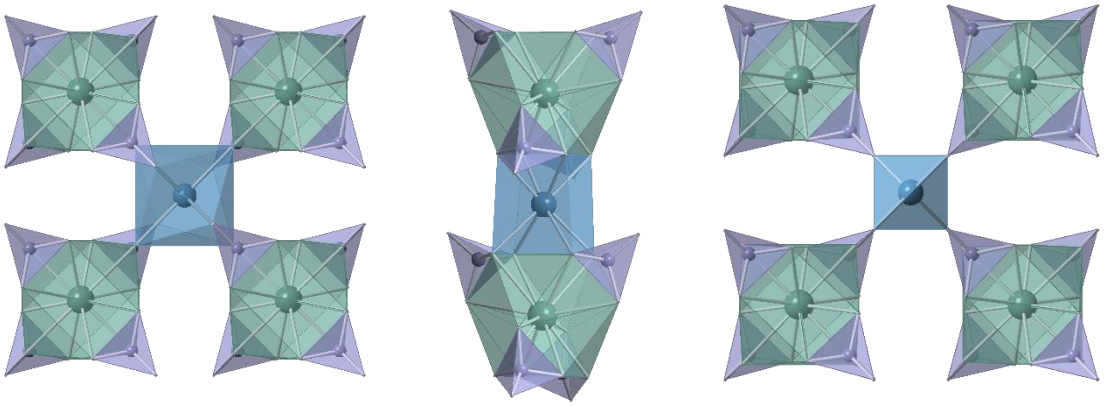

Figure S2 - Coordination polyhedra for the structure of $LiY(BH_4)_4$ in which Li ions are positioned at (a) 2*a*, (b) 2*b*, and (c) 2*e* Wyckoff sites; green : Y-H, violet: B-H, blue: Li-H.

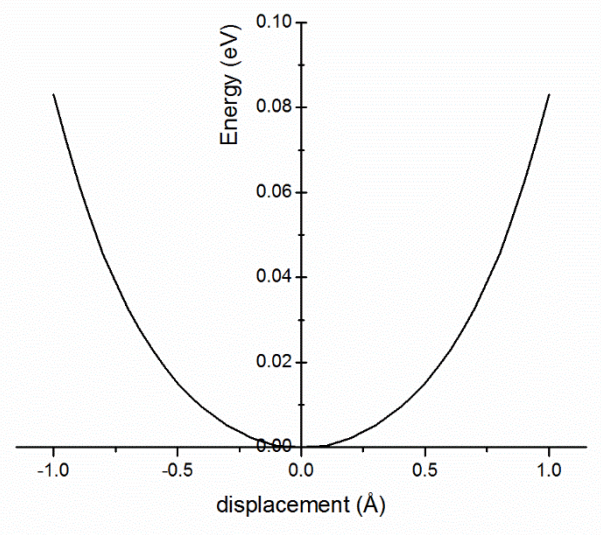

Figure S3 - Energy change upon displacing Na along *x* direction while other metal ions are frozen at the original positions.

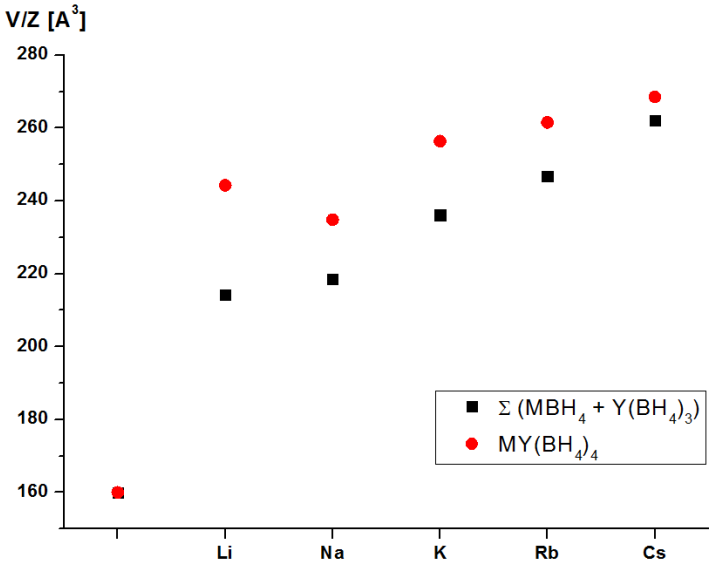

Figure S4 – Volume per formula unit of $MY(BH_4)_4$ (M= Li, Na, K, Rb, Cs) compared to the sum of unit cell volumes of $Y(BH_4)_3$ and MBH_4

a) **s1** (black), **s4** (blue) b) **s2** (black), **s5** (blue) c) **s3** (black), **s6** (blue)

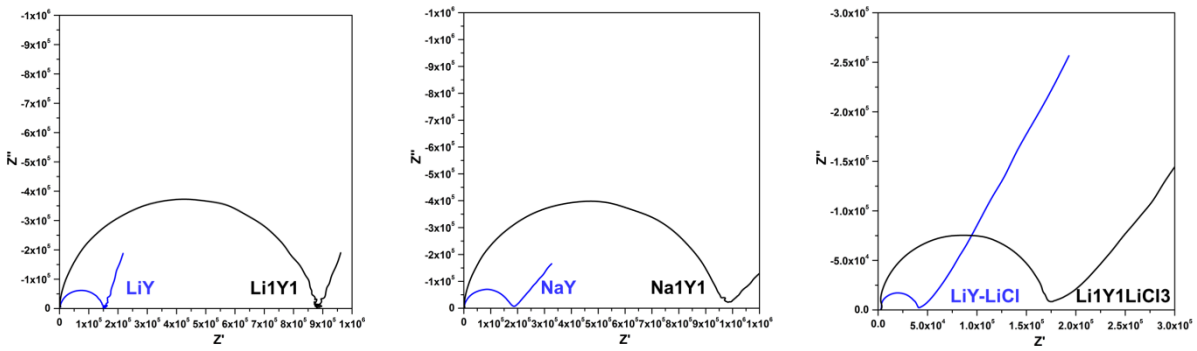

Figure S5 – Complex impedance spectra (Nyquist plot) of samples a) $Y(BH_4)_3$ – $LiBH_4$ (1:1), b) $Y(BH_4)_3$ – $NaBH_4$ (1:1) and c) YCl_3 – $LiBH_4$ (1:4) before (black) and after quenching (blue).

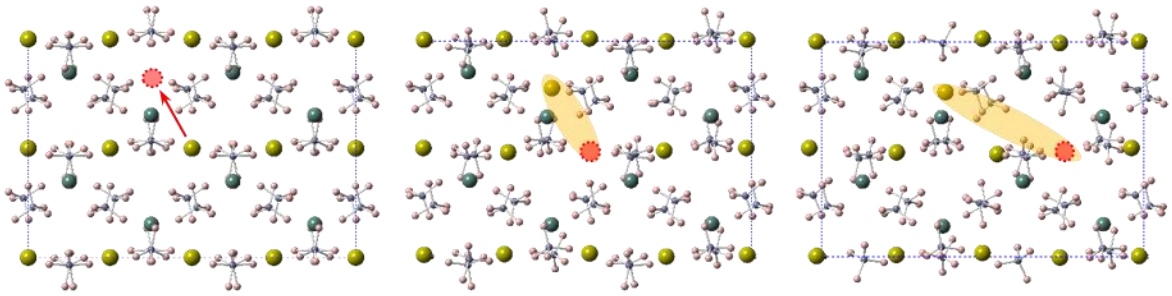

Figure S6 - (a) $NaY(BH_4)_4$ in the ideal configuration. The red circle marks a possible interstitial cite and a Frenkel defect can be generated by the movement of Na ion as indicated by the red arrow. A vacancy-interstitial pair located (b) nearby and (c) apart.

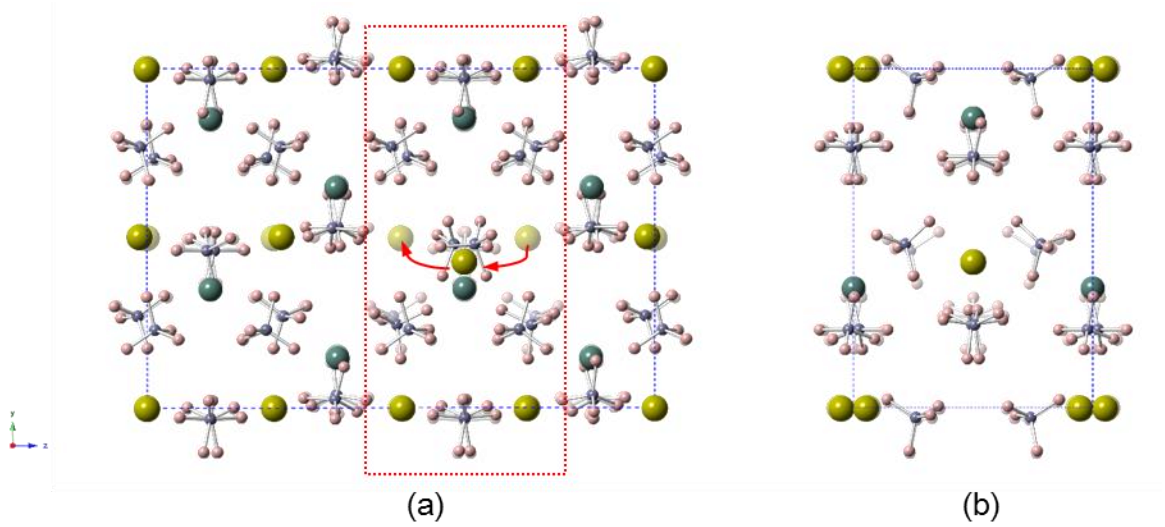

Figure S7 - (a) Vacancy hopping along the z-direction. Na ion is at the saddle point. The view direction is [100]. (b) Cross section image at the saddle point. The view direction is [001]. In both (a) and (b), the background translucent image shows the ideal configuration.

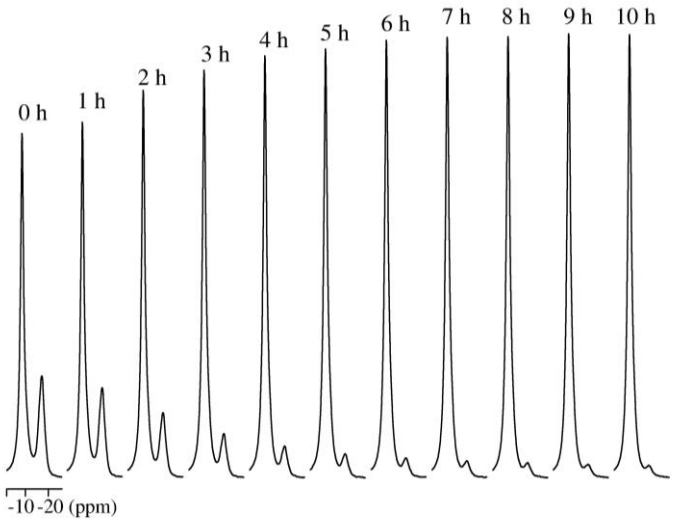

Figure S8. ^{23}Na MAS NMR spectra (14.1 T, ν_R = 8.0 kHz) of the central-transition region for $NaY(BH_4)_4$, following its thermal decomposition from shortly after its synthesis by quenching to 10 h of isothermal decomposition in the spinning NMR rotor (T = 24 ± 2 ^{o}C). The acquisition time for each spectrum was 15 min and every fourth spectrum is shown. The time indicates the beginning of the data acquisition.

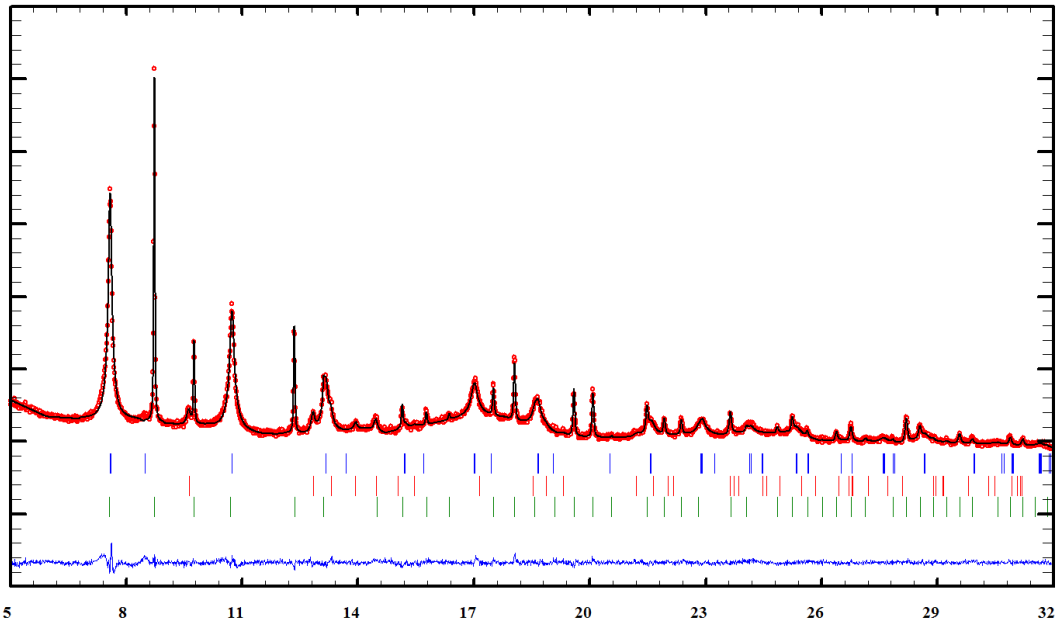

Figure S9 – High resolution PXD of $LiY(BH_4)_4$, obtained at room temperature, BLI11, Diamond, λ = 0.825770 Å, red circles: exp. data, black line: refined profile, blue line: difference pattern. Vertical dashes: reflexes of crystal phases: $LiY(BH_4)_4$ (top, R_{Bragg} = 5.3%), $LiBH_4$ (middle, R_{Bragg} = 1.5%), α-$Y(BH_4)_3$ (bottom, R_{Bragg} = 8.3%)

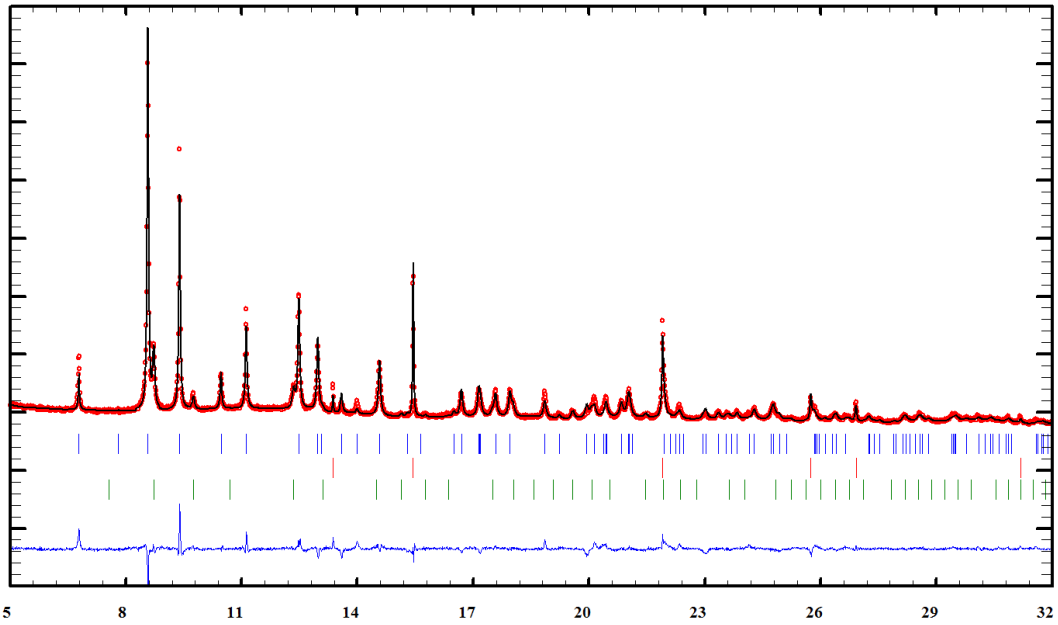

Figure S10 – High resolution PXD of $NaY(BH_4)_4$, obtained at room temperature, BLI11, Diamond, λ = 0.825770 Å, red circles: exp. data, black line: refined profile, blue line: difference pattern. Vertical dashes: reflexes of crystal phases: *C2221* - $NaY(BH_4)_4$ (top, R_{Bragg} = 8.7%), $NaBH_4$ (middle, R_{Bragg} = 10.4%), α-$Y(BH_4)_3$ (bottom, R_{Bragg} = 7.9%)

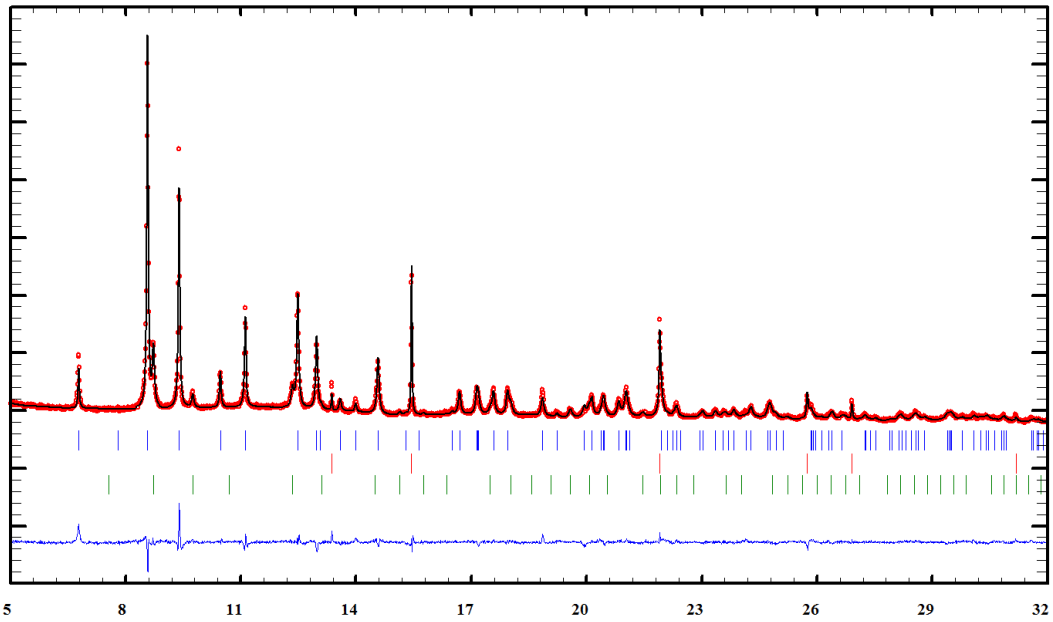

Figure S11 - High resolution PXD of $NaY(BH_4)_4$, obtained at room temperature, BLI11, Diamond, λ = 0.825770 Å, red circles: exp. data, black line: refined profile, blue line: difference pattern. Vertical dashes: reflexes of crystal phases: *Cmcm* - $NaY(BH_4)_4$ (top, R_{Bragg} = 7.7%), $NaBH_4$ (middle, R_{Bragg} = 12.3%), α-$Y(BH_4)_3$ (bottom, R_{Bragg} = 7.3%).