Supplementary Information.

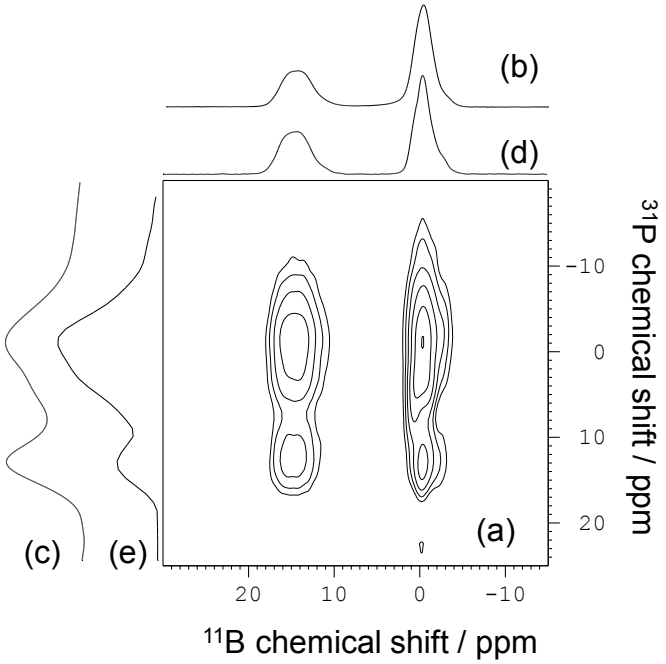

Fig.1 : (a) 2D $^{11}B/^{31}P$ correlation map obtained with the D-HMQC sequence on the $45Ag_2O$-$35B_2O_3$-$20P_2O_5$ samples obtained with ultra-fast quenching condition, accompanied with the 1D ^{11}B (b) and ^{31}P (c) MAS-NMR spectra and the horizontal (d) and vertical (e) 2D projections.

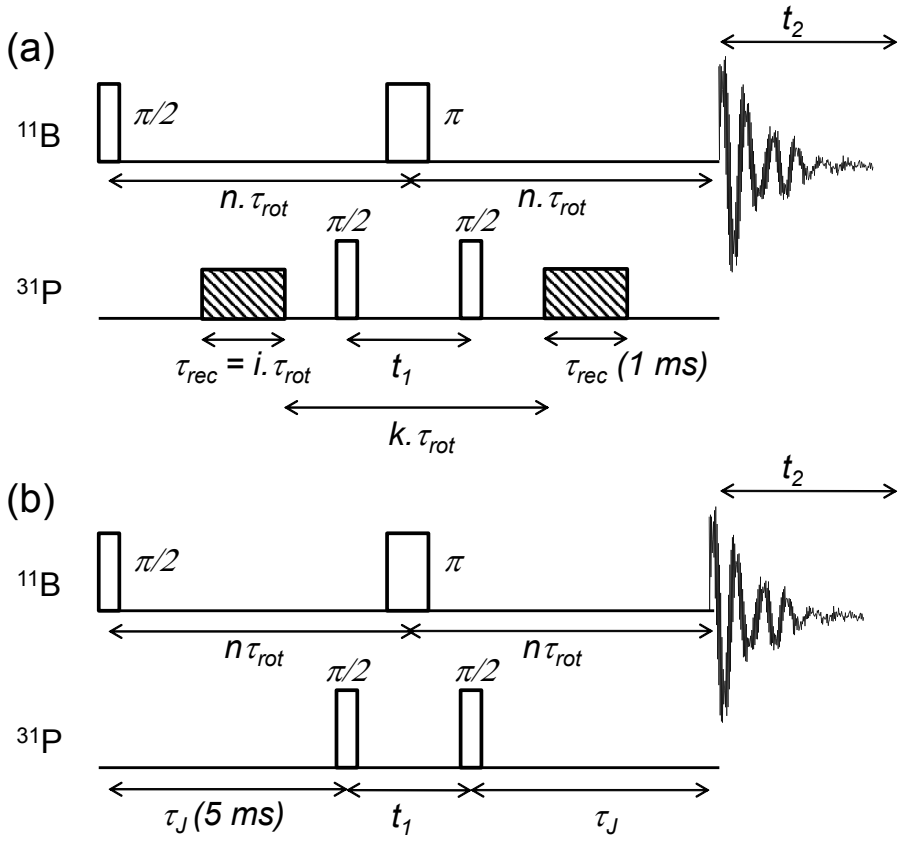

Fig.2: Dipolar (a) and scalar (b) ^{11}B(^{31}P) HMQC pulse sequences.

Tab.1: ^{31}P NMR parameters: chemical shift ($\delta_{iso,}$ +/- 0.1 ppm), full width at half maximum (fwhm +/- 0.2 ppm), relative proportions (rel. prop., +/- 2%) and assignment.

Sample	P^x	δiso / ppm	fwhm / ppm	rel. prop. / %	Qn
Li-ufq	P^1	-7.2	10.3	59.5	Q^0_2
	P^2	0.3	7.3	33.2	Q^0_1
	P^3	-16.1	11.8	6.4	Q^0_3
	P^4	10.0	3.7	0.8	Q^0_0
Na-ufq	P^1	-4.8	10.2	59.5	Q^0_2
	P^2	3.2	6.9	38.2	Q^0_1
	P^3	-14.8	11.8	2.3	Q^0_3
Na-sq	P^1	-4.2	10.2	60.8	Q^0_2
	P^2	3.6	7.1	37.1	Q^0_1
	P^3	-14.8	11.8	1.1	Q^0_3
K-ufq	P^1	-7.5	9.3	54.3	Q^0_2
	P^2	0.8	6.6	44.8	Q^0_1
	P^3	-11.7	11.7	0.9	Q^0_3
Ag-sq	P^1	-2.0	8.9	34.0	Q^0_2
	P^2	4.3	11.9	30.5	Q^0_1
	P^3	-12.1	12.4	8.0	Q^0_3
	P^4	13.5	5.8	24.0	?
	P^5	28.7	5.5	2.5	Q^0_0