

Supporting Information

Network Structure and Dissolution Properties of Phosphate-Doped Borosilicate Glasses

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Table S1. ^{23}Na MAS NMR fitting parameters for sample P4

δ_{iso} (ppm)	C_Q (MHz)	η_Q	Int. (%) ^c
2.46(0.3)	2.54(0.05)	0.6(0.2)	13(5)
-11.3(0.2) ^a	28.3(1) ^b		87(5)

^aPeak position (ppm)^bPeak width (ppm)^c Int. (%) = Integrated intensity**Table S2.** Fitting parameters used in the deconvolution of ^{31}P MAS NMR spectra

	P^0			P^1			$P^2_{\text{nB(Al)}}$			$\text{Na}_4\text{P}_2\text{O}_7$		
	δ_{iso} (ppm)	FWHM ^a	(%) ^b	δ_{iso} (ppm)	FWHM ^a	(%) ^b	δ_{iso} (ppm)	FWHM ^a	(%) ^b	δ_{iso} (ppm)	FWHM ^a	(%) ^b
P1	15.7(0.5)	3.6(1)	2(1)	3.4(0.3)	7.4(0.5)	69(5)	-6.5(0.5)	10.3(1)	29(5)	**	**	**
P2	14.5(0.2)	3.6(0.5)	11(2)	3.3(0.3)	7.2(0.3)	68(3)	-6.7(0.5)	10.4(1)	21(3)	**	**	**
P3	14.5(0.2)	3.1(0.2)	24(2)	2.6(0.3)	3.1(0.3)	51(8)	-6.5(1)	10.4(2)	9(4)	5.6(0.6)	3.1(0.5)	16(6)
P4	15.3(0.2)	3.5(0.3)	6(2)	2.4(0.5)	4.9(1.5)	65(15)	-6.3(1.5)	10.4(2)	8(4)	5.6(1)	4.2(1.5)	21(10)
P4-Mo3	12.3(0.5)	4.4(1)	3(2)	-0.1(0.5)	8.1(2)	64(20)	-6.2(3)	11.3(3)	19(15)	5.8(1)	4.9(2)	13(8)

^aFWHM = Peak width (ppm)^b(%) = Integrated intensity (%)

Table S3. ^{27}Al MAS NMR fit parameters

	$^{[4]}\text{Al}$			$^{[5]}\text{Al}$			$^{[6]}\text{Al}$		
	δ_{iso} (ppm) (± 0.2)	FWHM ^a (± 1)	Int. (%) ^b	δ_{iso} (ppm) (± 0.2)	FWHM ^a (± 0.5)	Int. (%) ^b	δ_{iso} (ppm) (± 0.2)	FWHM ^a (± 2)	Int. (%) ^b
P0	56.9	13.7	81(3)	14.3	5.8	19(3)	**	**	**
P1	56.3	13.9	84(2)	14.4	5.3	16(2)	**	**	**
P2	56.2	14.0	84(2)	14.4	5.3	16(2)	**	**	**
P3	56.4	14.1	90(1)	14.6	5.6	10(1)	**	**	**
P4	54.9	14.1	84(2)	14.1	5.4	16(2)	**	**	**
P4-Mo3	54.2	14.7	79(2)	14.4	5.9	15(1)	-6.1	14.9	6(2)

^aFWHM = Peak width (ppm)^bInt. (%) = Integrated intensity**Table S4.** ^{29}Si MAS NMR fit parameters

	Q^3		Q^4	
	Peak max (ppm)	Int. (%) ^a	Peak max (ppm)	Int. (%) ^a
P0	-89(2)	63(17)	-101(3)	37(17)
P2	-92(5)	41(14)	-102(3)	59(14)
P4	-93(2)	10(10)	-102(1)	90(10)
P4-Mo3	**	**	-105	100

^aInt. (%) = Integrated Intensity

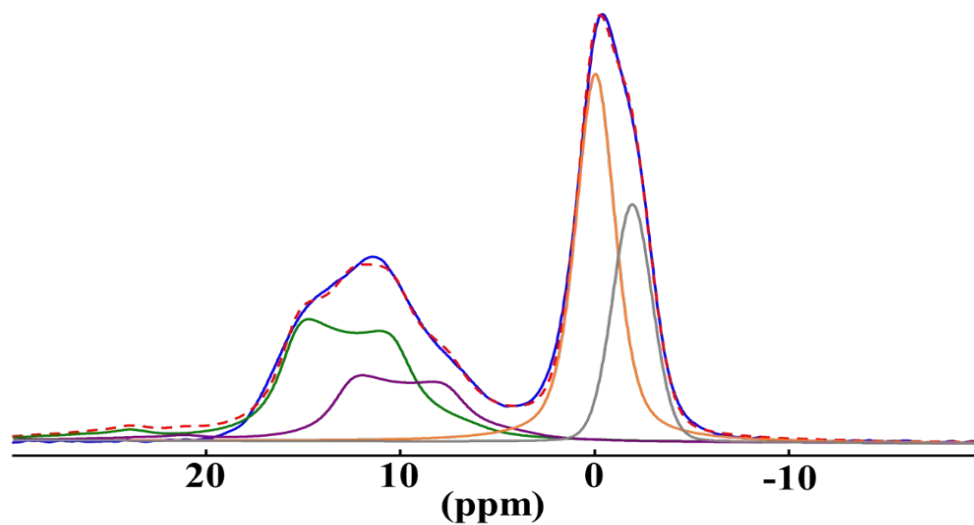


Figure S1. Deconvolution of ^{11}B MAS NMR spectrum of sample P0. Green, magenta, orange, and grey components represent $^{[3]}\text{B}_{\text{non-ring}}$, $^{[3]}\text{B}_{\text{ring}}$, $^{[4]}\text{B}_{3\text{Si}}$ and $^{[4]}\text{B}_{4\text{Si}}$ units, respectively.

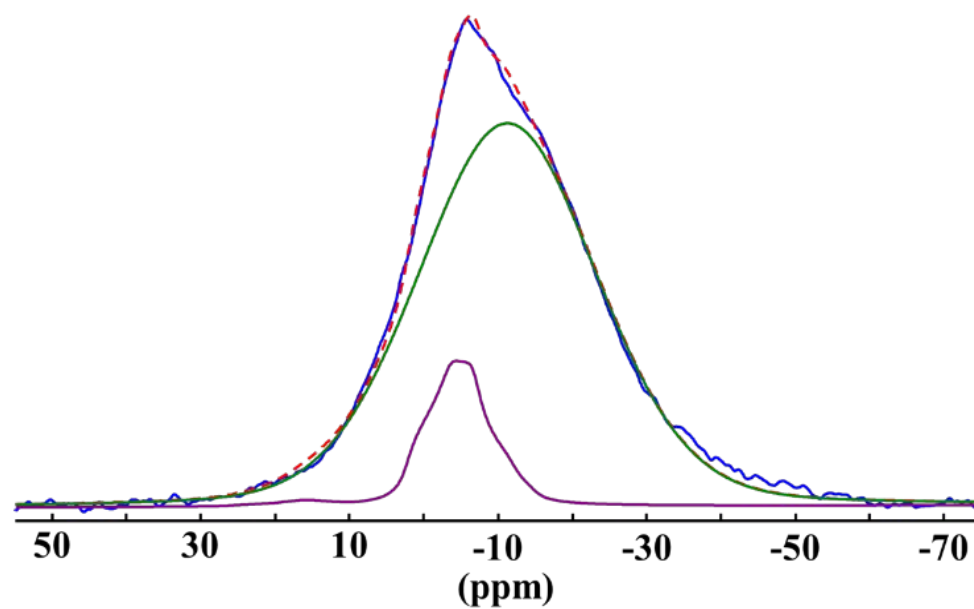


Figure S2. Deconvolution of the ^{23}Na MAS NMR spectrum of P4 representing glassy (green) and poorly-crystalline $\text{Na}_4\text{P}_2\text{O}_7$ (magenta) phases.

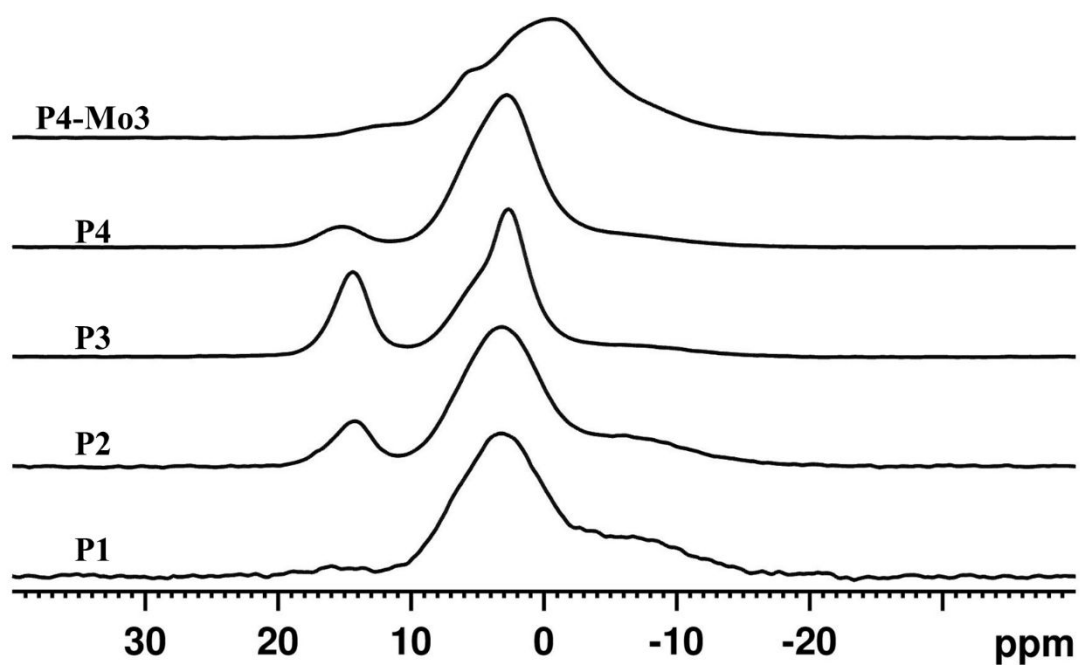


Figure S3. ^{31}P MAS NMR spectra of glasses

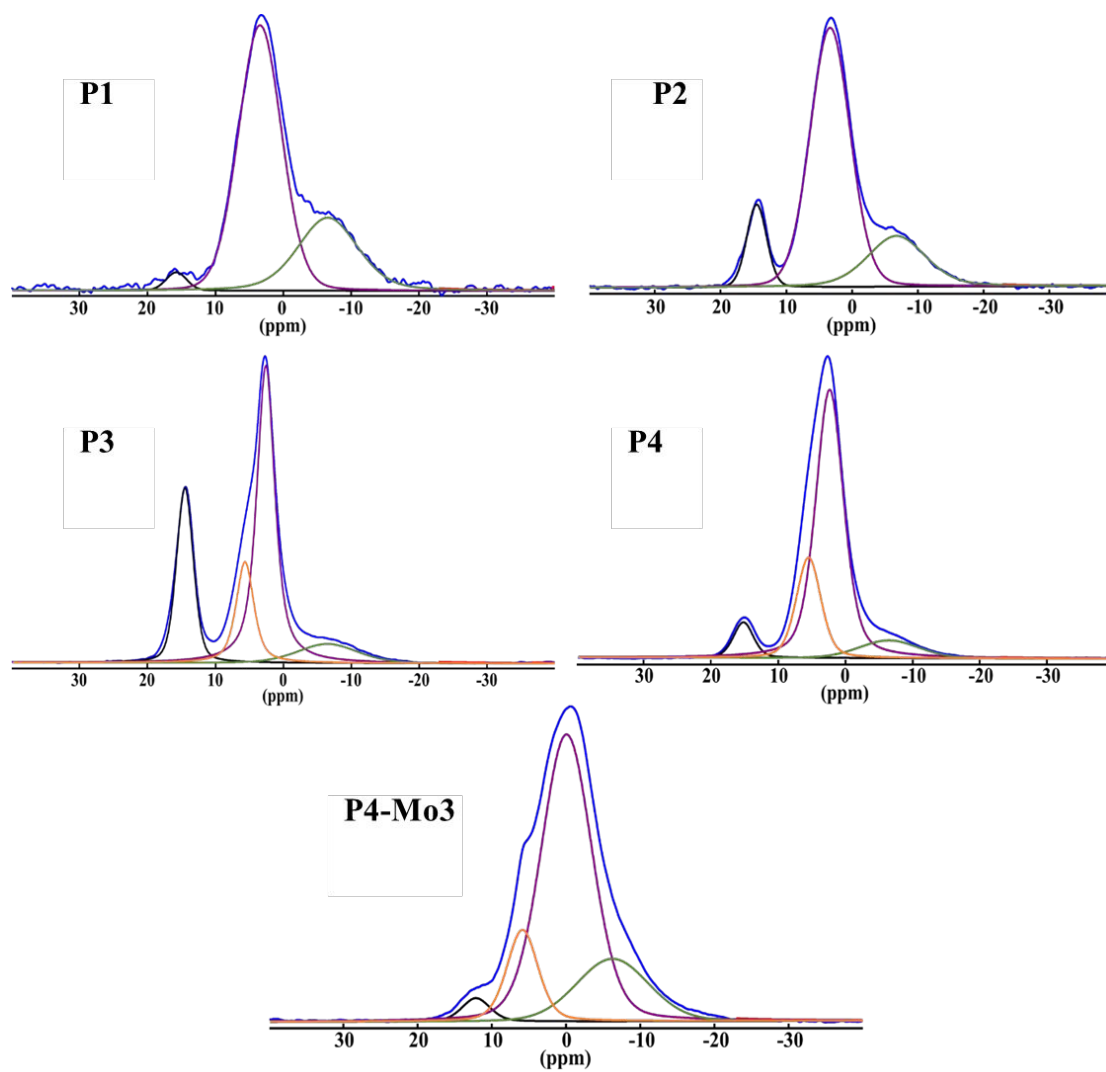


Figure S4. Deconvolution of ^{31}P MAS NMR spectra. Blue is the experimental spectrum and components in black, orange, purple and green represent P^0 , P^1 , $\text{P}^2_{\text{nB(Al)}}$ and poorly crystalline $\text{Na}_4\text{P}_2\text{O}_7$, respectively.

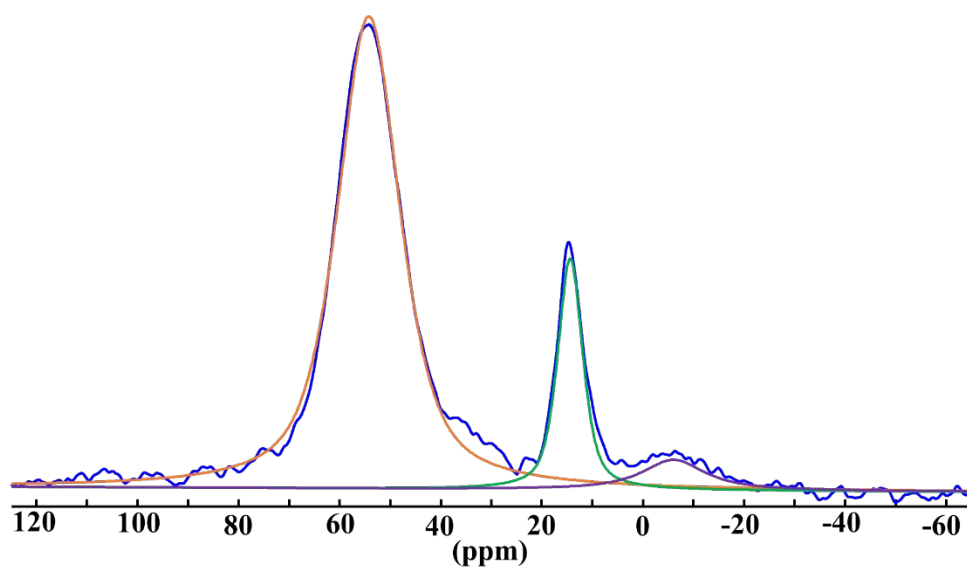
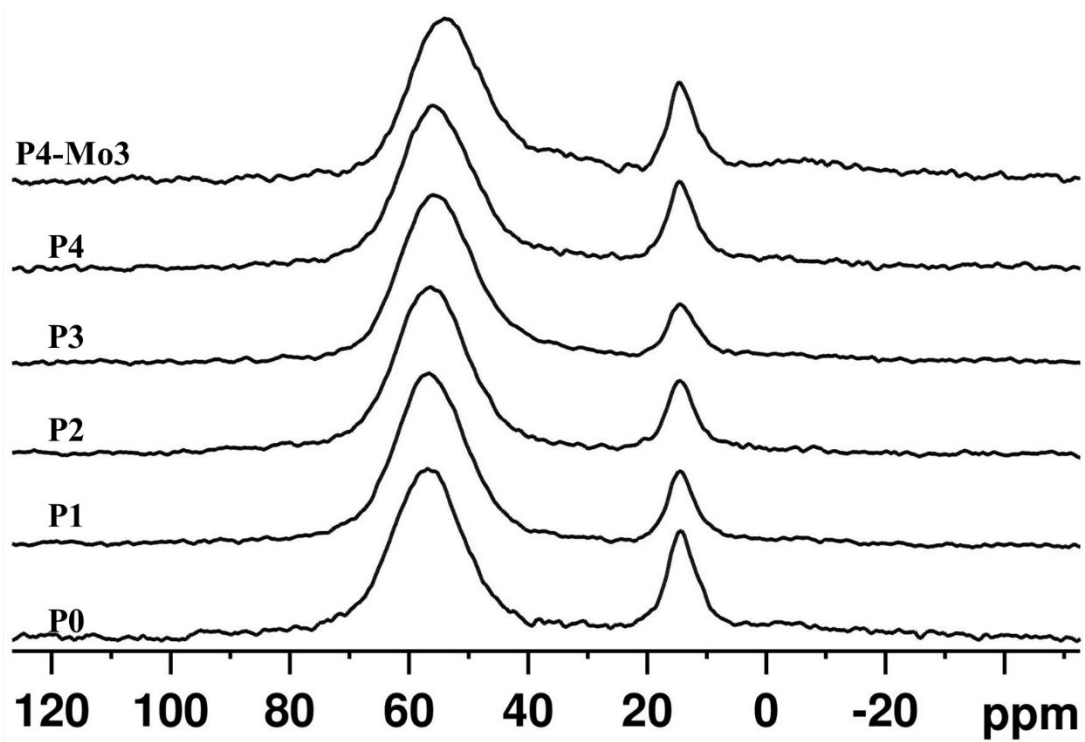


Figure S5. ^{27}Al MAS NMR spectra of glasses (top) and deconvolution of ^{27}Al MAS NMR spectrum of P4-Mo3, where orange, green and purple components represent ^{41}Al , ^{51}Al and ^{61}Al units, respectively.

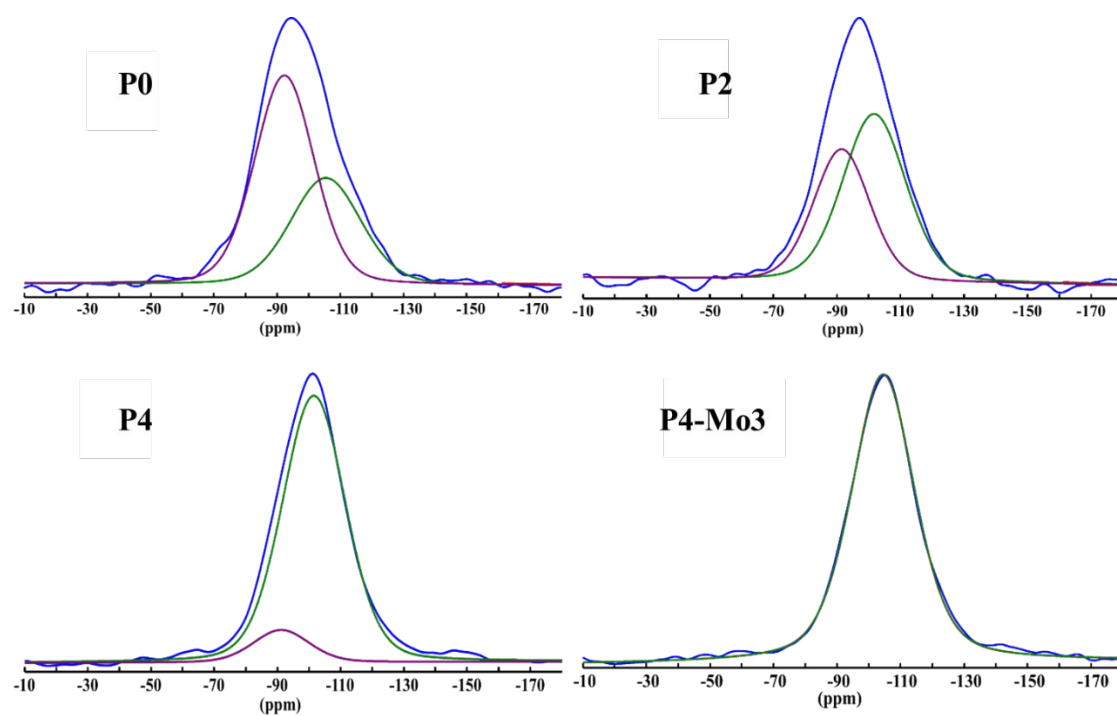


Figure S6. Deconvolution of ^{29}Si MAS NMR spectra. The subspectral components in purple and green represent Q^3 and Q^4 units, respectively.

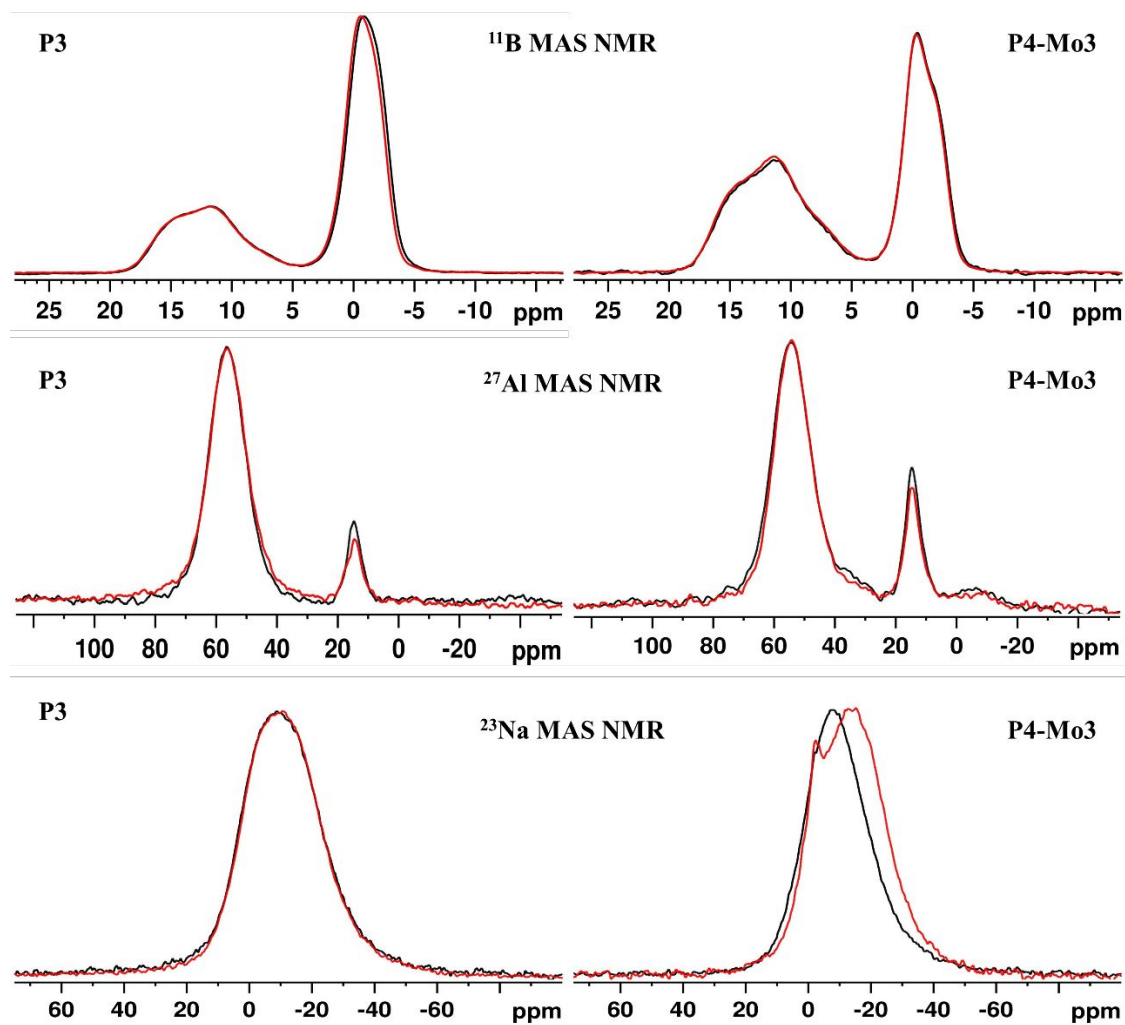


Figure S7. ^{11}B , ^{27}Al and ^{23}Na MAS NMR spectra of P3 and P4-Mo3 before (black) and after (red) dissolution.

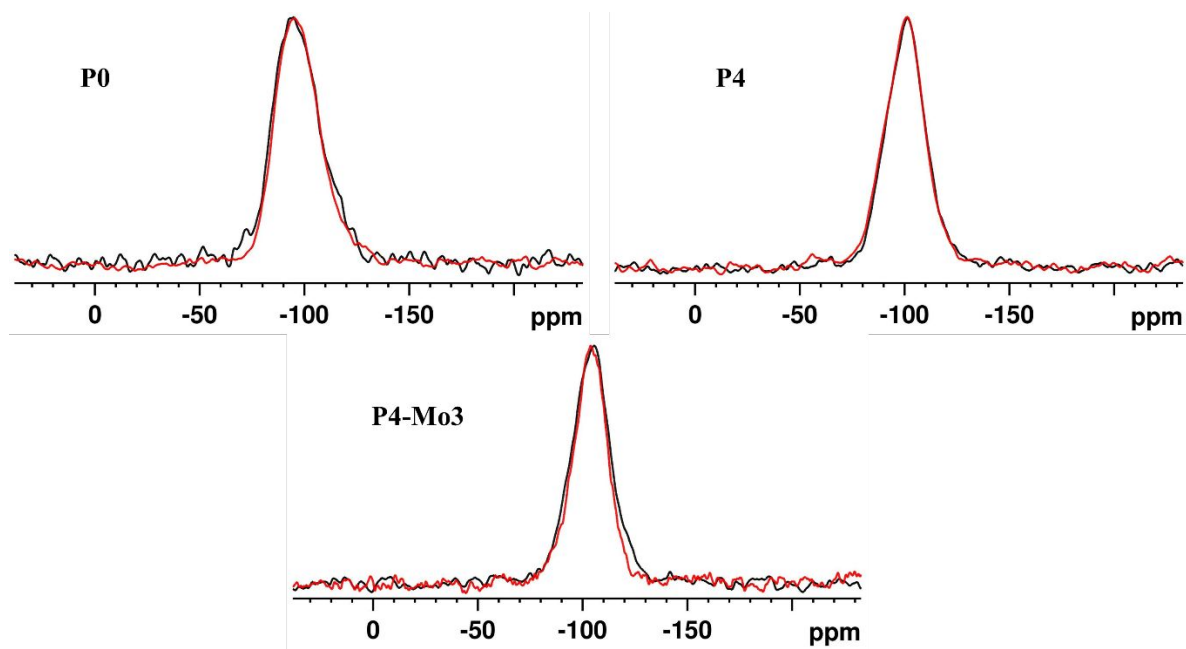


Figure S8. ^{29}Si MAS NMR spectra before (black) and after (red) dissolution

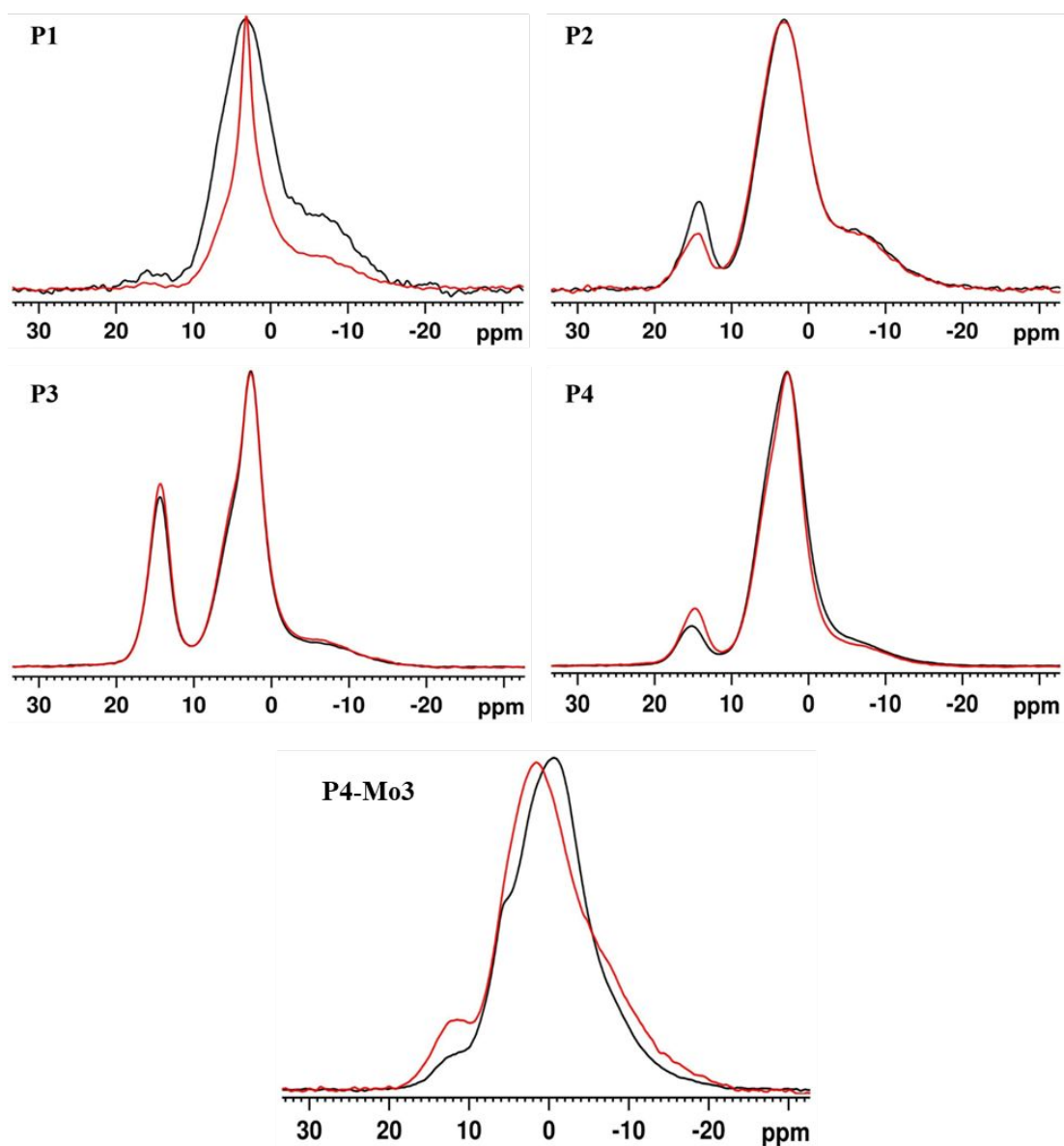


Figure S9. An overlay of ^{31}P MAS NMR spectra before (black) and after (red) the dissolution.

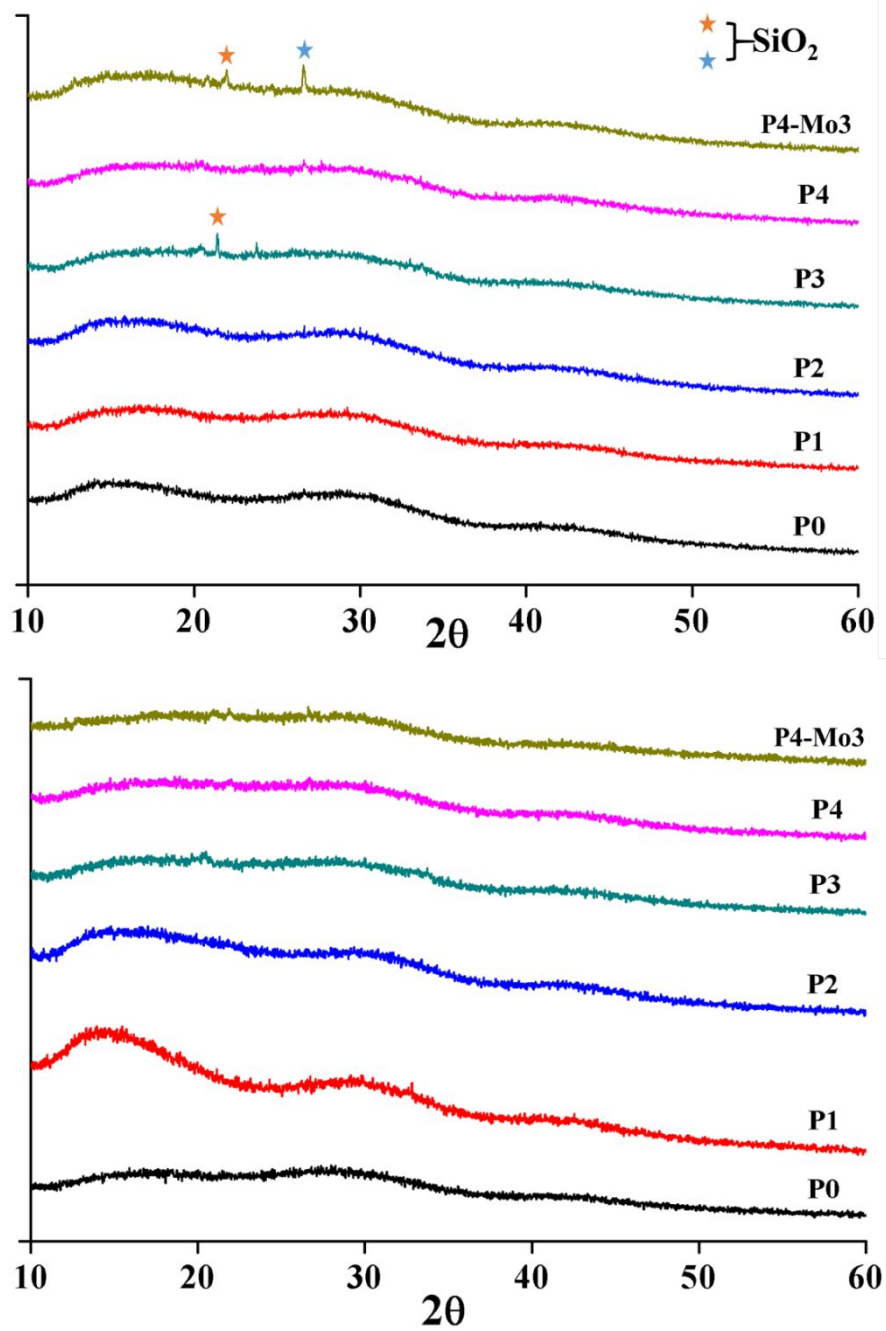


Figure S10. X-ray diffractograms before (top) and after (bottom) dissolution. The orange and blue stars represent reflections from the SiO_2 phases, cristobalite and quartz, respectively.

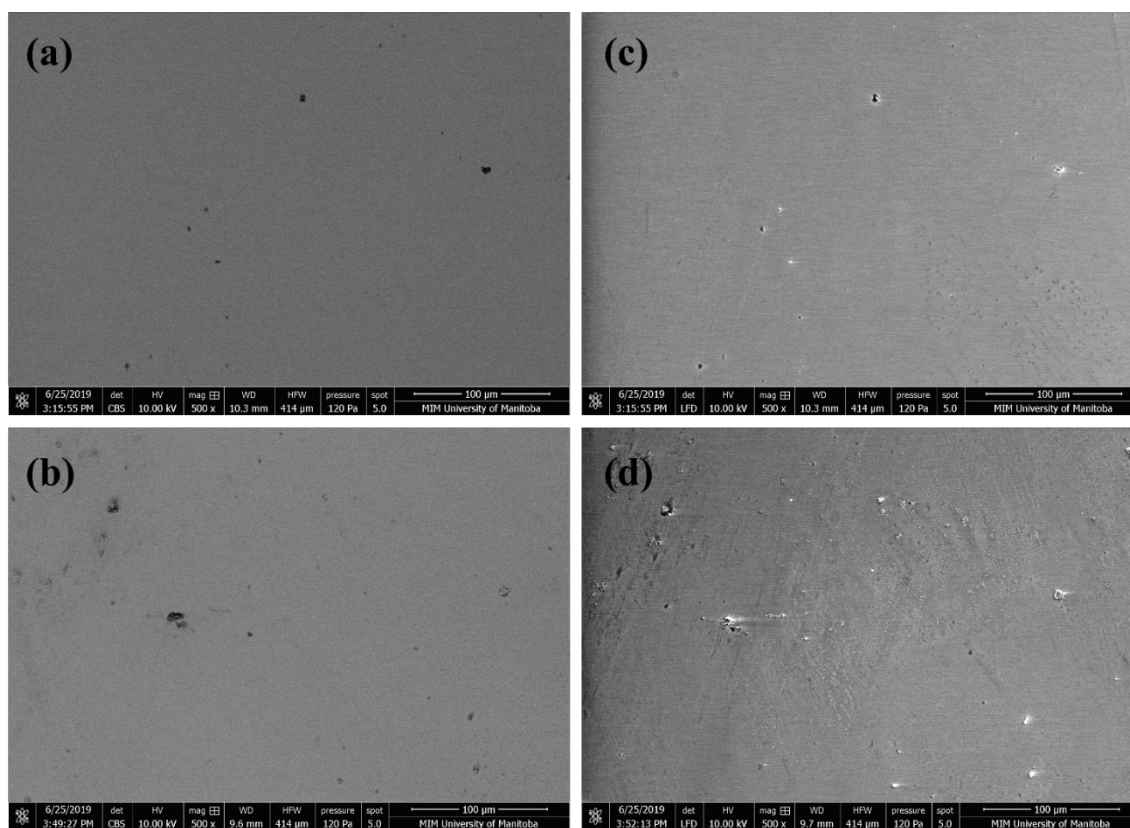


Figure S11. SEM images (500x magnification) of glasses prior to dissolution: (a) BSE image of P0, (b) BSE image of P4, (c) SE image of P0, (d) SE image of P4.

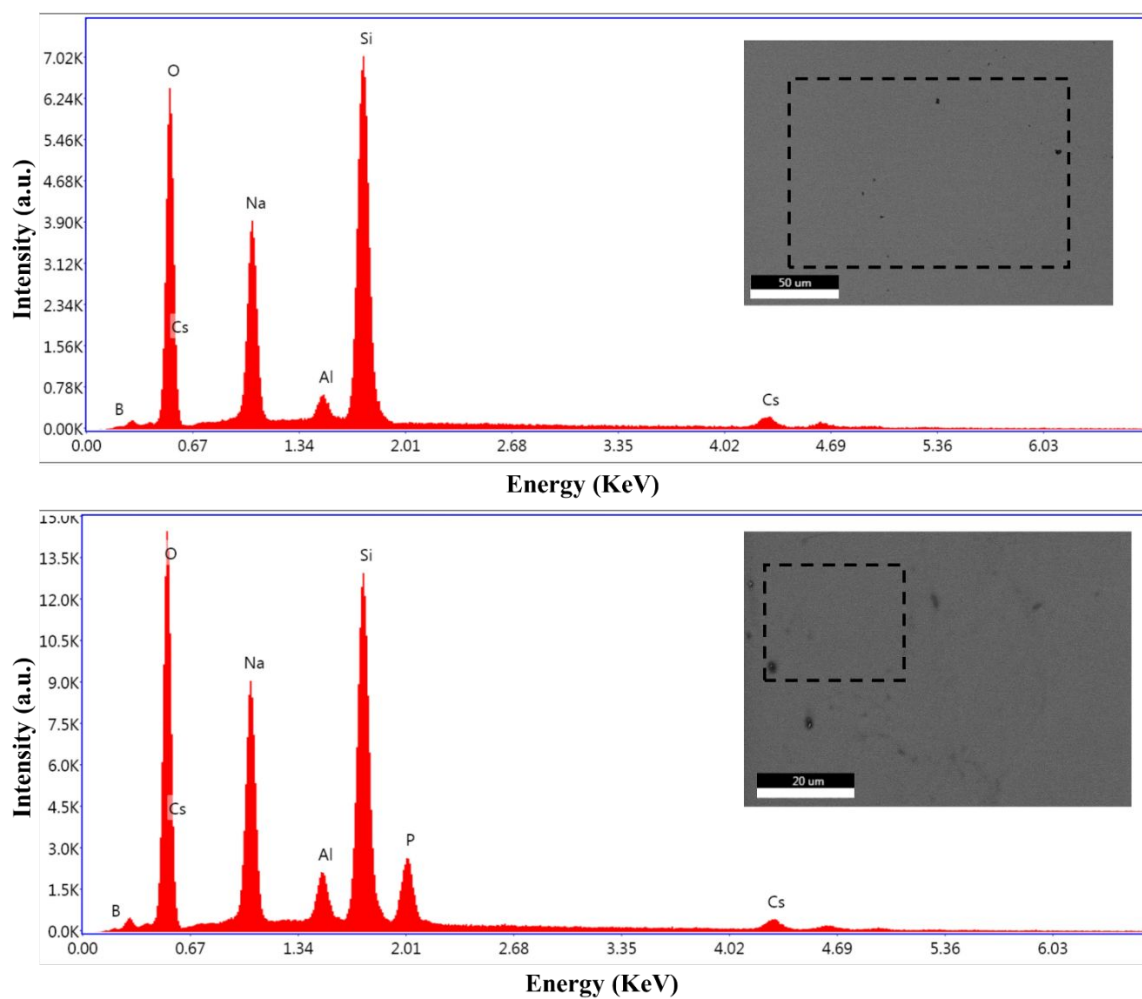


Figure S12. EDS spectra of glasses P0 and P4 with their corresponding BSE images. The dotted rectangles show the analyzed areas.

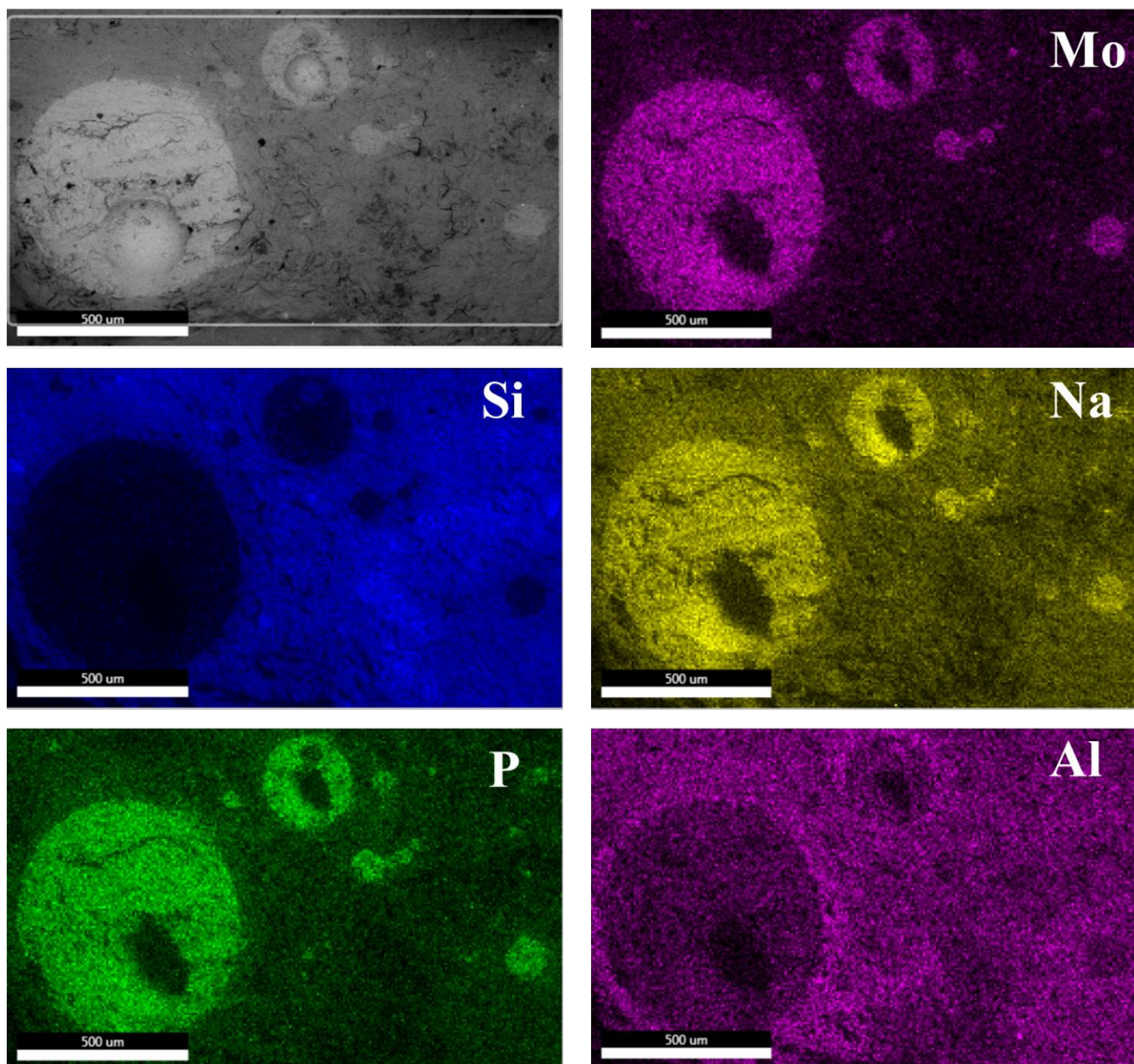


Figure S13. BSE image of a cross-section of P4-Mo3 and the element maps showing the distribution of elements in the mapped area.

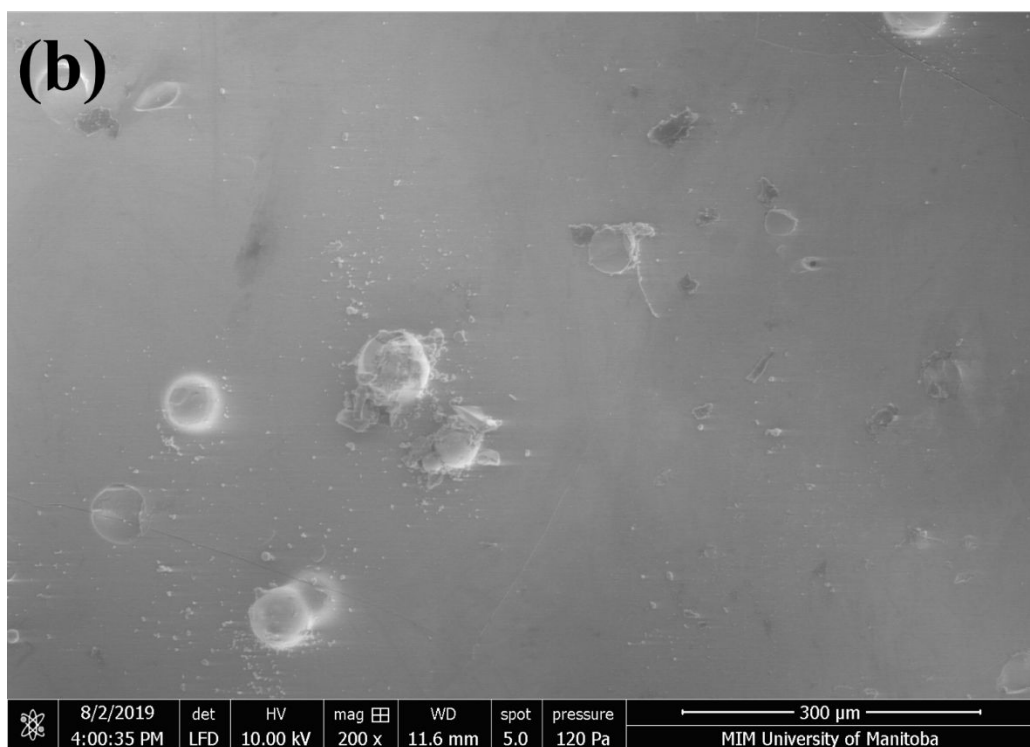
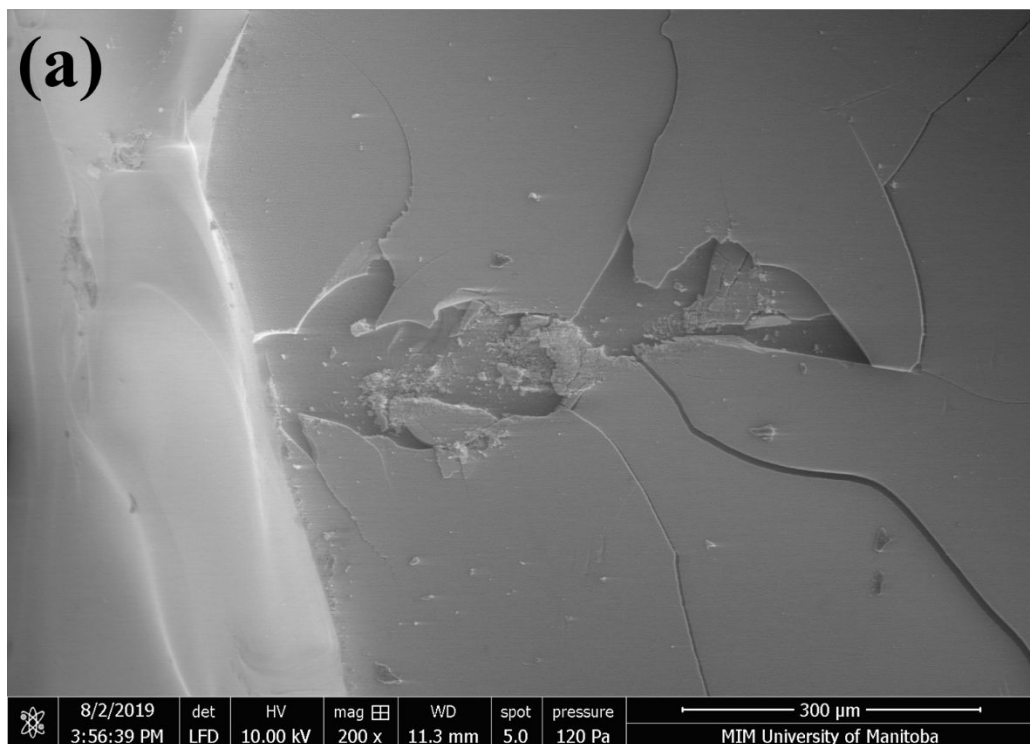


Figure S14. BSE images of the surfaces of (a) P4 and (b) P4-Mo₃ after dissolution.

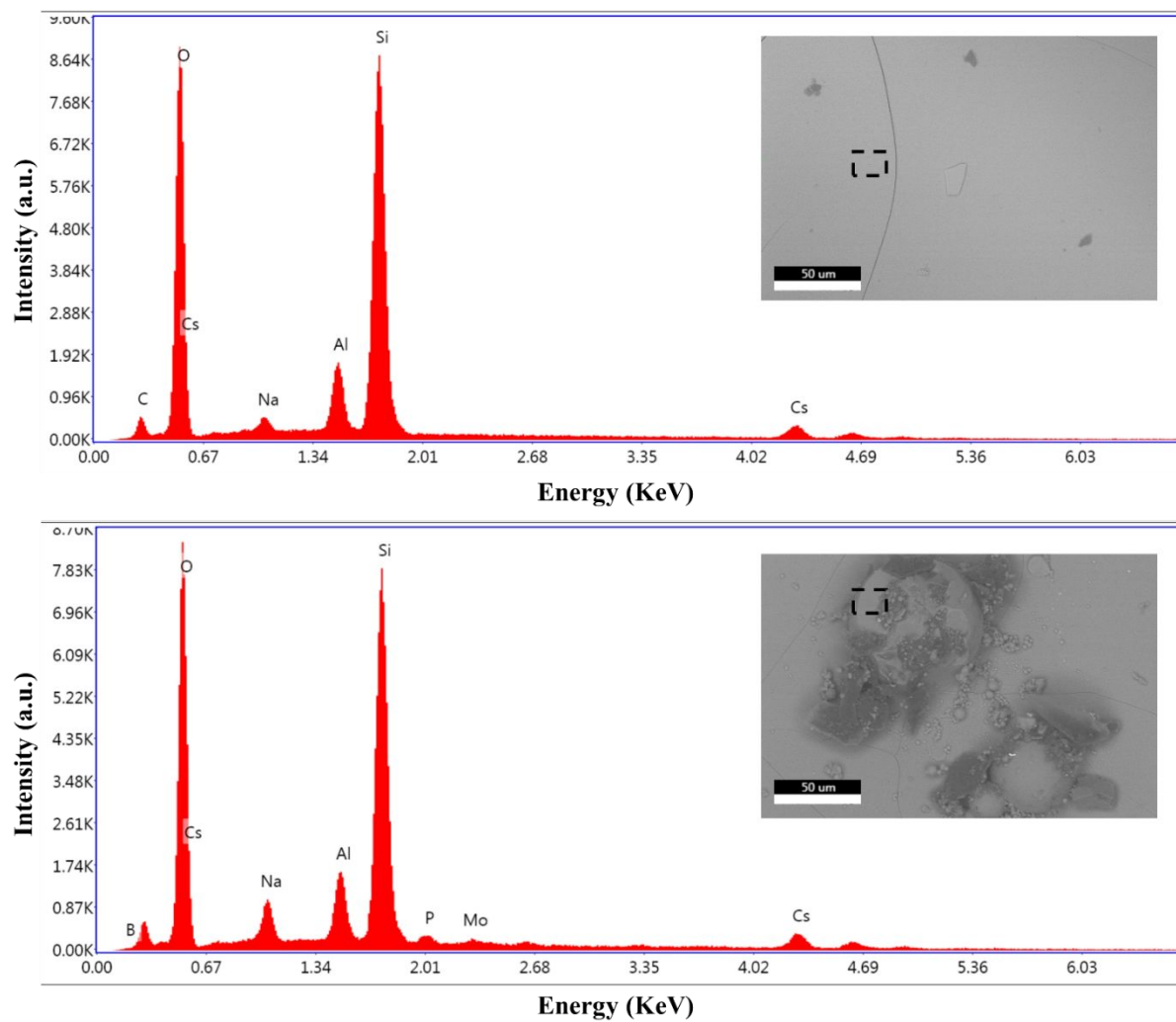


Figure S15. EDS spectra of the surfaces of glasses P4 (top) and P4-Mo3 (bottom) after dissolution.

The analyzed areas are marked with a dotted square in the BSE images shown.

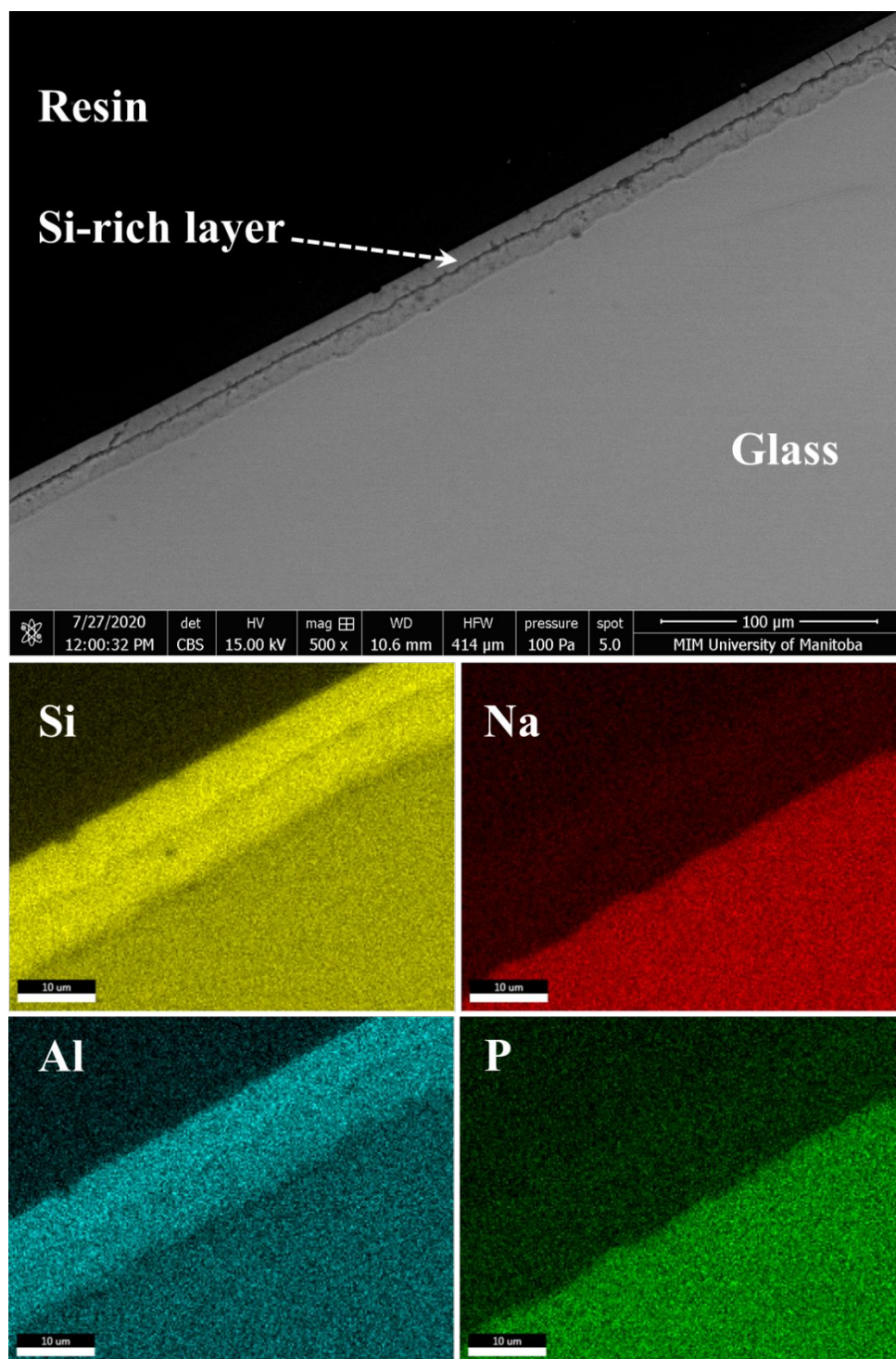


Figure S16. Back-scattered electron image of a cross-section of sample P4 after dissolution, and element maps of the Si-rich layer deposited on the glass surface