

Supplementary material

Structure of Zn and Na borophosphate glasses by X-ray and neutron diffraction

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Table S1. Batch compositions and mass densities of the investigated glass samples. The labels zbp xx and nbp xx indicate the glasses with ZnO or Na₂O, respectively. For the sample zbp14, the composition and mass density finally used as taken from [17] are given in parentheses. The reasons for using these parameters for zbp14 are explained in the text.

Sample label	ZnO (Na ₂ O) (mol%)	B ₂ O ₃ (mol%)	P ₂ O ₅ (mol%)	Mass density (g cm ⁻³)	Remarks
zbp01	50	0	50	2.84	series Zn(PO ₃) ₂ -BPO ₄
zbp02	44.4	5.6	50	2.82	
zbp03	32	18	50	2.77	
zbp04	25	25	50	2.745	
zbp05	60	0	40	3.26	series O/P = 3.25
zbp06	55.5	2.5	42	3.13	
zbp07	50	5.6	44.4	2.99	
zbp08 nbp08	44.25	8.75	47	2.88 2.40	
zbp09	37.5	12.5	50	2.79	
zbp10	30	16.7	53.3	2.71	
zbp11	20	22.2	57.8	2.66	
zbp12	57.33	5.6	37.07	3.33	series O/P = 3.5
zbp13 nbp13	45.83	12.5	41.67	3.075 2.44	
zbp14	50.0 (54.0)	50.0 (46.0)	0	(3.49)	ZnO-B ₂ O ₃ glass

Table S2. Parameters of the Gaussian functions used for fitting the first-neighbor peaks of the X-ray and neutron $T(r)$ functions. The values with asterisks were fixed in the fits. The parameters of the B–O peak of the borophosphate glasses were fixed with $N_{\text{BO}} = 4$, $r_{\text{BO}} = 0.147$ nm with an fwhm (full width at half maximum) = 0.0013 nm but are given in the table only for sample zbp02.

Sample	Atom pair	Coord. number	Distance (nm)	fwhm (nm)	Total coord.	Mean distance
zbp01	P–O	2.00	0.1495	0.010	3.88±0.15	0.1547±0.0015
		1.88	0.1603	0.012		
	Zn–O	3.70	0.1942	0.016	4.30±0.25	0.1965±0.0015
		0.60	0.211	0.022		
		0.10	0.230*	0.025*		
O–O	4.00*	0.2510	0.020			
zbp02	B–O	4.0*	0.147*	0.013*	3.90±0.15	0.1549±0.0015
	P–O	2.20	0.1502	0.011		
		1.70	0.1610	0.013		
	Zn–O	3.50	0.1940	0.014	4.30±0.25	0.1972±0.0015
		0.80	0.211	0.022		
		0.20	0.230*	0.025*		
O–O	0.432*	0.241*	0.018*	3.85*	0.2515	
	3.85*	0.2515	0.020			
zbp03	P–O	2.50	0.1510	0.011	3.90±0.15	0.1547±0.0015
		1.40	0.1614	0.013		
	Zn–O	3.55	0.1940	0.014	4.40±0.20	0.1973±0.0015
		0.85	0.211	0.020		
		0.40	0.230*	0.025*		
	O–O	1.28*	0.241*	0.018*	3.57*	0.252
3.57*		0.252	0.019			
zbp04	P–O	2.88	0.1518	0.011	3.85±0.15	0.1542±0.0015
		0.97	0.1615	0.013		
	Zn–O	4.00	0.1940	0.017	4.60±0.30	0.1963±0.0015
		0.60	0.212	0.020		
		0.60	0.224	0.025*		
	O–O	0.432*	0.241*	0.018*	3.85*	0.2515
3.85*		0.2515	0.020			
zbp05	P–O	2.45	0.1510	0.011	3.80±0.15	0.1546±0.0015
		1.35	0.1610	0.012		
	Zn–O	3.05	0.1943	0.017	4.10±0.25	0.1981±0.0015
		1.05	0.209	0.020		
		0.40	0.230*	0.025*		
O–O	3.69*	0.252	0.018			
zbp06	P–O	2.40	0.1513	0.011	3.60±0.15	0.1549±0.0015
		1.20	0.1620	0.013		
	Zn–O	3.10	0.1943	0.017	3.95±0.20	0.1979±0.0015
		0.85	0.212	0.020		
		0.40	0.230*	0.025*		
	O–O	0.22*	0.241*	0.018*	3.69*	0.252
3.69*		0.252	0.018			
zbp07	P–O	2.65	0.1515	0.011	3.80±0.15	0.1548±0.0015
		1.15	0.1625	0.013		
	Zn–O	3.30	0.1943	0.017	4.30±0.20	0.1981±0.0015
		1.00	0.212	0.020		
		0.20	0.230*	0.025*		
	O–O	0.46*	0.241*	0.018*	3.69*	0.252
3.69*		0.252	0.018			

Sample	Atom pair	Coord. number	Distance (nm)	fwhm (nm)	Total coord.	Mean distance
zbp08	P-O	2.60	0.1515	0.011	3.76±0.15	0.1547±0.0015
		1.16	0.1618	0.013		
	Zn-O	3.45	0.1941	0.016	4.30±0.20	0.1976±0.0015
		0.85	0.212	0.019		
	O-O	0.20	0.230*	0.025*		
		0.69*	0.241*	0.018*		
		3.69*	0.2515	0.020		
zbp09	P-O	2.50	0.1511	0.011	3.80±0.15	0.1544±0.0015
		1.30	0.1606	0.013		
	Zn-O	3.80	0.1940	0.016	4.50±0.20	0.1965±0.0015
		0.70	0.210	0.019		
	O-O	0.20	0.230*	0.025*		
		0.92*	0.241*	0.018*		
		3.69*	0.252	0.018		
zbp10	P-O	2.45	0.1512	0.011	3.75±0.15	0.1544±0.0015
		1.30	0.1605	0.012		
	Zn-O	3.90	0.1944	0.0165	4.65±0.25	0.1972±0.0015
		0.75	0.2115	0.0195		
	O-O	0.35	0.228	0.025*		
		1.16*	0.241*	0.018*		
		3.69*	0.252	0.020		
zbp11	P-O	2.70	0.1517	0.011	3.60±0.15	0.1540±0.0015
		0.90	0.1622	0.012		
	Zn-O	4.30	0.1945	0.017	5.70±0.50	0.1988±0.0020
		1.40	0.212	0.020		
	O-O	0.20	0.230*	0.025*		
		1.42*	0.240*	0.018*		
		3.69*	0.2515	0.019		
zbp12	P-O	2.85	0.1518	0.010	3.95±0.15	0.1546±0.0015
		1.10	0.1619	0.012		
	Zn-O	3.02	0.1950	0.017	4.02±0.20	0.1987±0.0015
		1.00	0.210	0.019		
	O-O	0.55	0.230*	0.025*		
		0.52*	0.241*	0.018*		
		3.43*	0.252	0.018		
zbp13	P-O	2.80	0.1515	0.0105	3.80±0.15	0.1544±0.0015
		1.00	0.1625	0.012		
	Zn-O	3.15	0.1945	0.017	4.20±0.20	0.1984±0.0015
		1.05	0.210	0.020		
	O-O	0.50	0.230*	0.025*		
		0.92*	0.241*	0.018*		
		3.69*	0.252	0.018		
nbp08	P-O	2.70	0.1515	0.0105	3.95±0.15	0.1550±0.0015
		1.25	0.1625	0.013		
	Na-O	1.50	0.224	0.016	4.5±0.3	0.238±0.003
		1.50	0.238	0.018		
	O-O	1.50	0.252*	0.022		
		0.69*	0.241*	0.018*		
		3.80*	0.2515	0.020		
nbp13	P-O	2.50	0.1511	0.011	3.80±0.15	0.1558±0.0015
		1.30	0.1606	0.013		
	Na-O	1.50	0.224	0.018	4.0±0.3	0.238±0.003
		1.50	0.240	0.022		
	O-O	1.00	0.255	0.025*		
		0.92*	0.241*	0.018*		
		3.69*	0.252	0.018		

Sample	Atom pair	Coord. number	Distance (nm)	fwhm (nm)	Total coord.	Mean distance
zbp14	B-O	2.10	0.140	0.010	3.30±0.15	0.1418±0.0015
		1.20	0.145	0.010		
	Zn-O	3.70	0.1977	0.0195	4.30±0.10	0.2001±0.0015
		0.60	0.215	0.022		
		0.30	0.230	0.025		
O-O	3.74*	0.239*	0.018			

Table S3. Selected parameters taken from [17] are used for the calculation of other parameters of the binary Zn borate glasses. The ZnO contents, mass densities, B-O coordination numbers (N_{BO}), and glass transition temperatures are taken from [17] while the number densities of atoms, packing densities, BC_{GFU} , and ratios of oxygens per B and Zn are calculated. The ratio O_{NB}/Zn is calculated according to Equation 7. Different from the BO_4 in the borophosphate glasses studied, the boron in the BO_3 units of the binary glasses forms some B- O_{NB} bonds, which is expressed by the ratio O_{NB}/B . BC_{GFU} is the average number of bridging corners per glass-forming unit.

ZnO content (mol%)	53.8	57.1	60.0	62.5	64.7	66.7
Mass density (g/cm ³)	3.490	3.582	3.667	3.748	3.815	3.889
Number density (atoms/nm ³)	93.7	92.8	92.2	91.6	91.0	90.7
Packing density (%)	55.32	54.79	54.34	54.01	53.61	53.42
B-O coordination number	3.29	3.26	3.23	3.20	3.17	3.13
Total ratio O/B	2.08	2.17	2.25	2.33	2.42	2.50
Ratio O_{NB}/B	0.88	1.07	1.27	1.47	1.66	1.87
Ratio O_{NB}/Zn	1.50	1.61	1.69	1.76	1.81	1.87
$BC_{GFU} = 2 O_B/B$	2.42	2.19	1.96	1.73	1.51	1.26
T_g (°C)	559	546	544	537	534	532

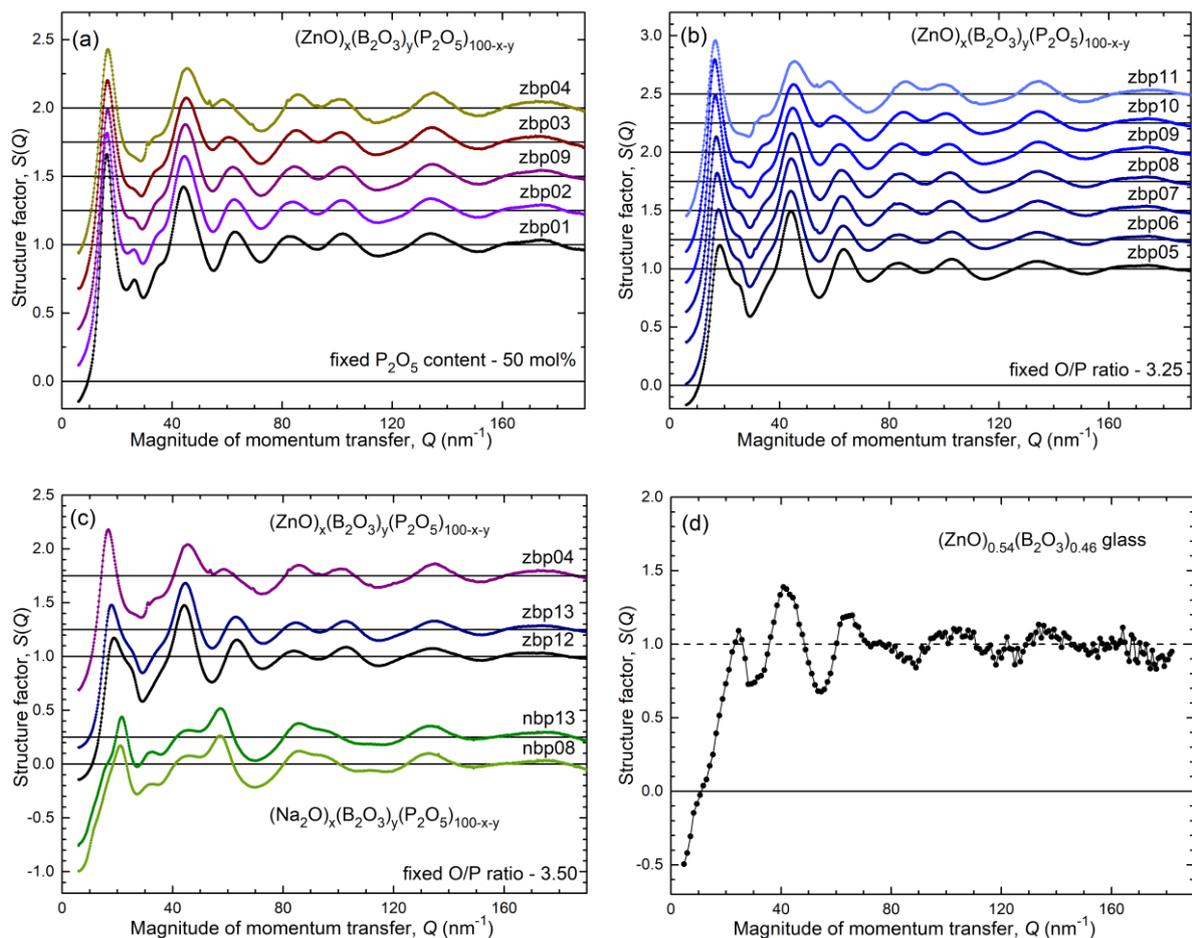


Figure S1. X-ray structure factors of three compositional series of Zn borophosphate glasses (a, b, c), two Na borophosphate glasses (c), and a binary Zn borate glass (d), the latter obtained with Ag K_{α} radiation. The $S(Q)$ factors are calculated according to Equation 1. The unphysical decrease of the intensities for $Q > 190 \text{ nm}^{-1}$ suggests omitting these data points.

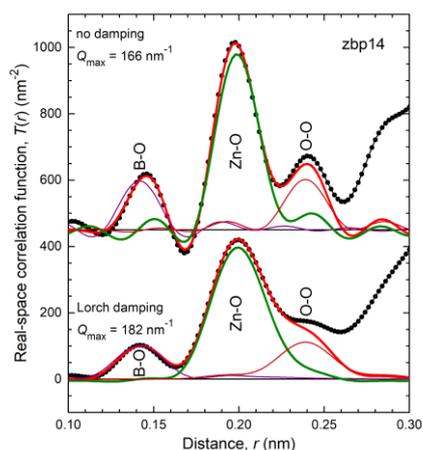


Figure S2. The X-ray correlation functions $T(r)$ of the Zn borate glass zbp14. The $T(r)$ functions are calculated with Lorch damping ($Q_{\text{max}} = 182 \text{ nm}^{-1}$) and without damping ($M(Q) = 1$, $Q_{\text{max}} = 166 \text{ nm}^{-1}$). The upper curves are shifted for clarity. The experimental $T(r)$ curves (black dots) are compared with the total model functions (thick red lines) and the partial Zn-O peaks (thick olive lines). The other partial model peaks are given with thin lines (B-O – purple; O-O – dark red).

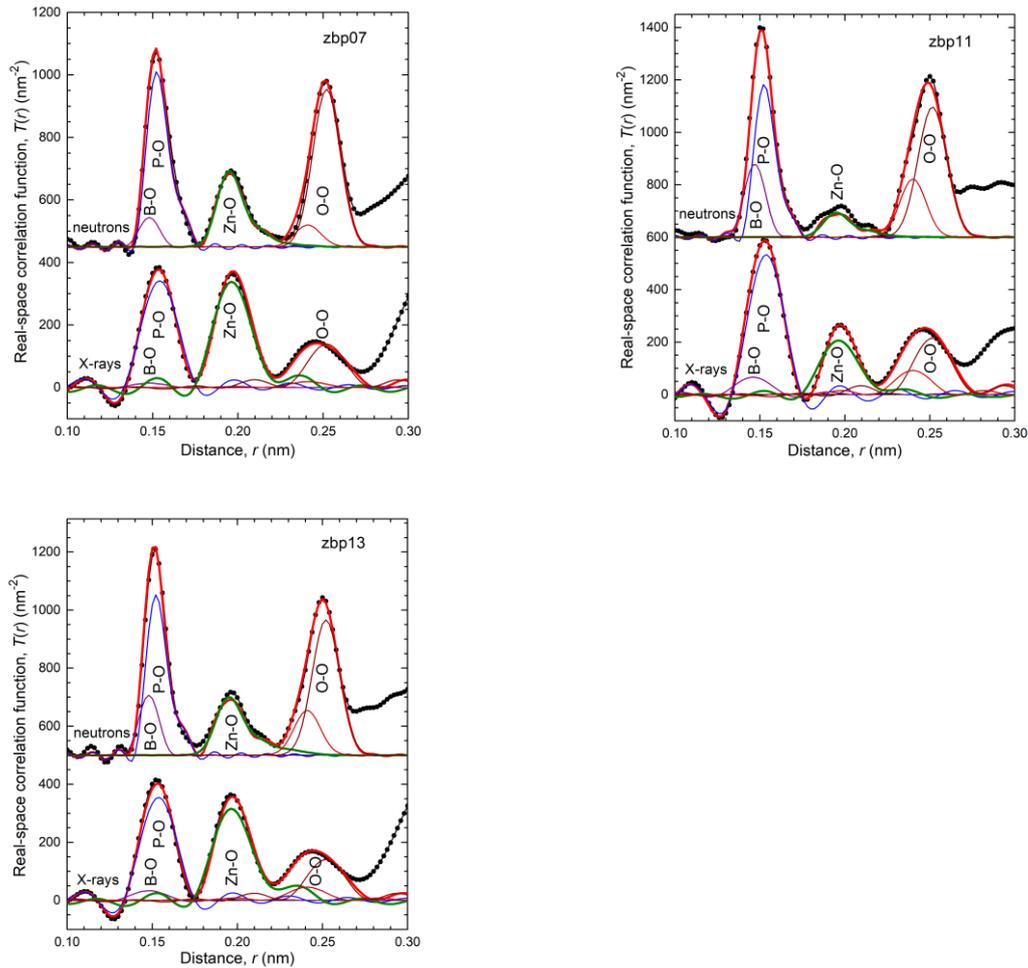


Figure S3. Neutron and X-ray correlation functions $T(r)$ of the samples zbp07, zbp11, and zbp13 obtained without damping ($M(Q) = 1$). The upper neutron curves are shifted for clarity. The experimental curves (black dots) are compared with the total model functions (thick red lines) and the partial Zn–O peaks (thick olive lines). The other partial model peaks are given with thin lines (B–O – purple; P–O – blue; O–O – dark red and brown). The two model O–O peaks belong to the different edge lengths of the BO_4 and PO_4 units.

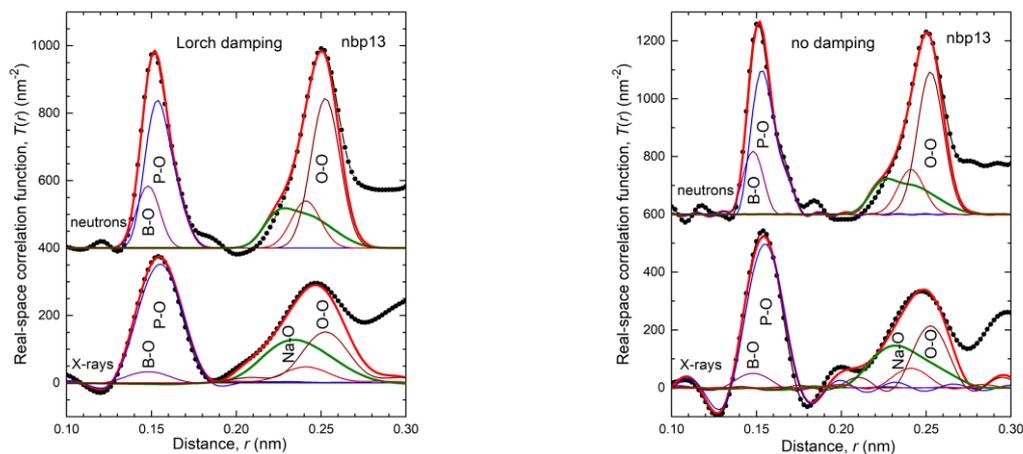


Figure S4. Neutron and X-ray correlation functions $T(r)$ of the Na borophosphate glass nbp13 obtained with Lorch damping ($Q_{\text{max}} = 500$ or 200 nm^{-1}) and without damping ($M(Q) = 1$, $Q_{\text{max}} = 400$ or 183 nm^{-1}). The upper neutron curves are shifted for clarity. The experimental curves (black dots) are compared with the total model functions (thick red lines) and the partial Na–O peaks (thick olive lines). The other partial model peaks are given with thin lines (B–O – purple; P–O – blue; O–O – dark red and brown). The two model O–O peaks belong to the different edge lengths of the BO_4 and PO_4 tetrahedra.

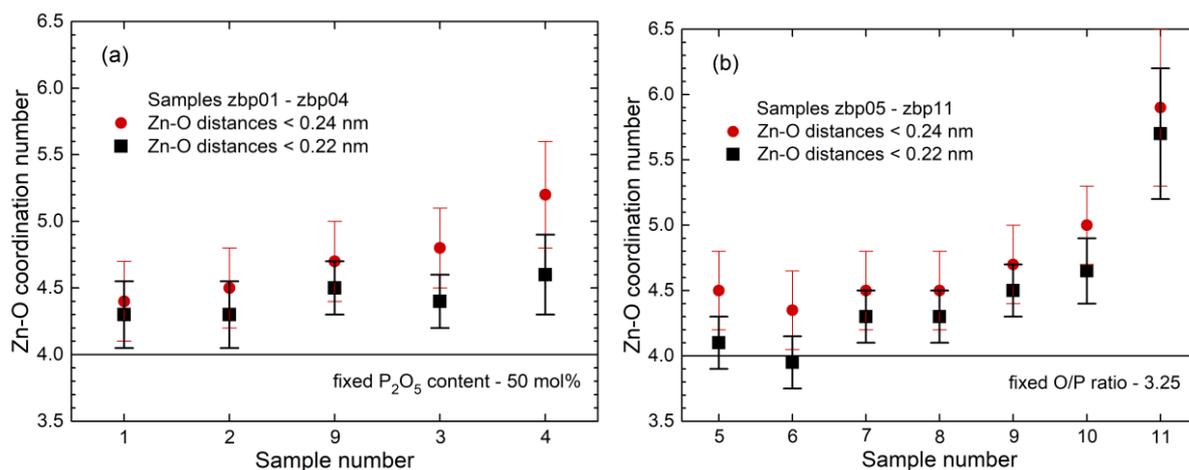


Figure S5. Evolution of the Zn–O coordination numbers for two series of the Zn borophosphate glasses: (a) constant P_2O_5 content of 50 mol%, (b) constant O/P ratio of 3.25. The black squares denote the values according to typical bond lengths. The red circles are values that include some a little longer contributions. The values of the samples zbp06 and zbp11 are considered outliers.

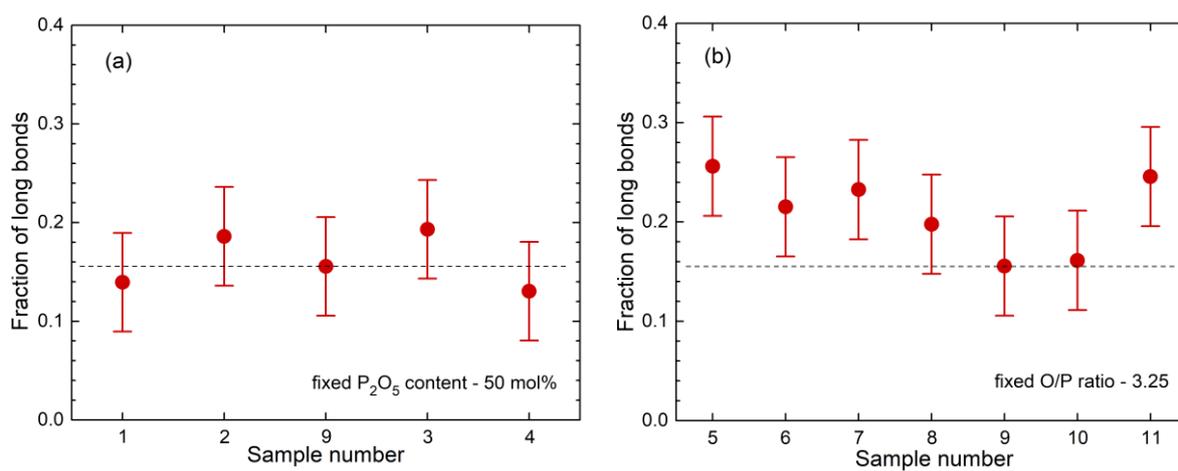


Figure S6. Fractions of the long Zn–O bonds (~ 0.212 nm) for two series of the Zn borophosphate glasses: (a) constant P_2O_5 content of 50 mol%, (b) constant O/P ratio of 3.25.

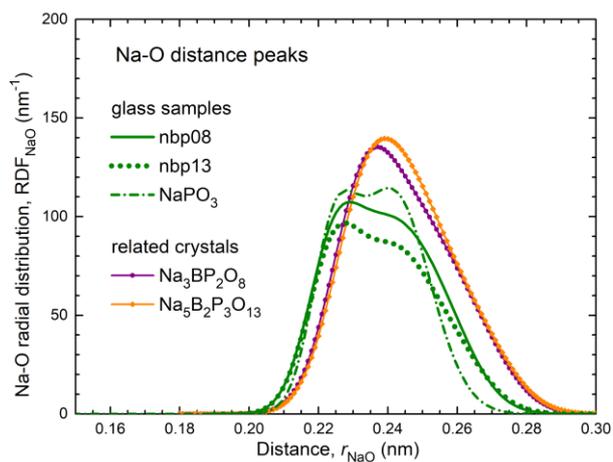


Figure S7. Model peaks of the Na–O first-neighbor distances of the glass samples nbp08 (solid line), nbp13 (dotted line), and NaPO₃ (dash-dotted line) as obtained from Gaussian fitting in comparison with peaks that are calculated for two related crystals (lines with symbols).

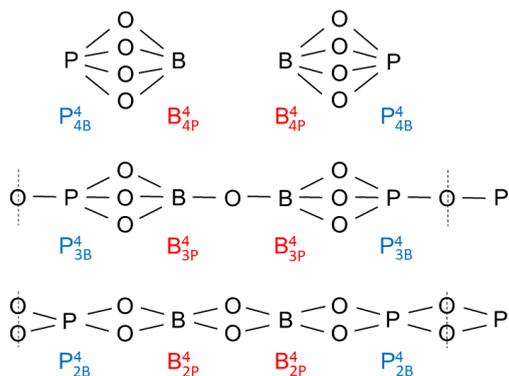


Figure S8. Illustration of the rearrangement of groups as given with Equation 4. The formation of B–O–B bridges is accompanied by a polymerization of the phosphate network.