## Supporting information

To examine the convergence of system size, we carried out three simulations of composition  $15Na_2O-15Al_2O_3-70SiO_2$  in NA series and  $5\%P_2O_5-95\%[15Na_2O-15Al_2O_3-70SiO_2]$  in PNA series with increasing system size from 1,000, 3,000, to 6,000 atoms in simulation box. The

Qn distribution of both silicon and aluminum are provided in SF 1(a~d). The  $Q_{Si}^n$  and  $Q_{Al}^n$  distribution

are generally converged for systems containing 3000 and 6000 atoms although  $Q_{Al}^3$  species concentration is slightly higher for the system with 6000 atoms. Ring size distributions are also analyzed as shown in SF 1(e~f). Both for NA and PNA, ring size distribution converges for systems with 3000 and 6000 atoms while the smaller systems with 1000 atoms show some discrepancies. In our study, there are 58 compositions to be studied, each with three parallel simulations (that is 174 simulations in total). Considering both the accuracy of glass model and computational efficiency, all the results and discussion reported here are based on the simulation cell with 3000 atoms.





SF 1. System size effect on structural data including  $Q_{Si}^{n}$  distribution of (a) NA, (b) PNA,  $Q_{Al}^{n}$  distribution of (c) NA, (d) PNA, and ring size distribution of (e) NA and (f) PNA



SF 2.  $Q_x^n$  distribution for (a) Si, (b) Al, (c) P and (d)  $\overline{Q}_x^n$  and network connectivity (NC) for LAP glass compositions



SF 3.  $Q_x^n$  distribution for (a) Si, (b) Al, (c) P and (d)  $Q_x^n$  and network connectivity (NC) for MAP glass compositions



SF 4.  $Q_x^n$  distribution for (a) Si, (b) Al, (c) P and (d)  $\overline{Q}_x^n$  and network connectivity (NC) for HAP glass compositions



SF 5. Total correlation function of Na-O for (a) MAP and (b) HAP glass compositions





SF 6. Total correlation function of T-Na for (a) LAP, (b) MAP, and (c) HAP glass compositions



SF 7. Morphology screenshots of typical simulation samples, (a) MAP-P0, (b) MAP-P7, (c) HAP-P0, (d) HAP-P7. The screenshots show the bulk size with around 34 Å in length 6.8 Å for thickness. Color indications: red-O, blue-Si (stick model); bluegreen tetrahedra-Al, purple tetrahedra-P, yellow ball-Na



SF 8. Degree of preferred connection of Si-O-Si linkages for NA and PNA compositions with various Al/Na ratios