Electronic Supplementary Information:

Local Structures and Al/Si Ordering in Lanthanum Aluminosilicate Glasses Explored by Advanced ²⁷Al NMR Experiments and Molecular Dynamics Simulations

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S1. Fictive-Temperature Estimations

Additional MD simulations were performed with variable cooling rates (q_c) of $\{1, 5, 10, 20\}$ K/ps for the two glass compositions La^{1.03}_{0.63}(2.21) and La^{0.33}_{0.59}(2.54) (see Table S1). Each quench-rate $q_c = \Delta T / \Delta t$ employed a fixed $\Delta T = 100$ K, whereas Δt was adjusted. Besides involving a smaller number of 3500 atoms, the computational procedures were identical to those described in detail in section 6.3. We used the MD trajectories between the initial (3500 K) and final (300 K) temperatures to estimate the fictive temperature (T_f) as follows: Each trajectory was sampled every 2 ps, of which the last few data-points that feature the best equilibration were used to obtain the instantaneous temperature and average configurational energy, E(T). The latter was calculated as the sum over all interatomic potential energies in the ensemble, whereas the temperature was determined from the mean kinetic energy. The T and E(T) values were further averaged over four independent simulation results, only differing in their initial atom configurations (see section 6.3).

Figure S1(a) shows an example of E(T) plotted versus temperature for the La^{0.33}_{0.59}(2.54) sample with $q_c=1$ K/ps. As expected, the slope of the curve alters around the melt-to-glass transition due to the difference in heat capacity between the two phases.^{S1-S3} Our choice of monitoring E(T) for detecting the first-order phase transition stems from the use of NVT ensembles; $T_{\rm f}$ -determinations are normally performed under conditions of constant pressure and therefore typically involve more physically intuitive variables, such as the sample volume.^{S2,S3} The fictive temperature was determined as the intersection point between two straight lines, each one extrapolated from high (low) temperatures of the melt (glass), as illustrated in Fig. S1(a). The bearings from cooling-rate variations on the E(T) curves, and hence the $T_{\rm f}(q_c)$ dependence, is conveyed in Figs. S1(b, c). The $T_{\rm f}$ associated with each $E(T, q_c)$ curve was extracted, which resulted in a spread of $T_{\rm f}$ -values between 1567 K at $q_c=1$ K/ps and 1720 K at $q_c=20$ K/ps.

Figure S1(d) plots $\log_{10} \{q_c\}$ against the inverse temperature, which as expected reveals a linear relationship^{S1,S3,S4} with a correlation coefficient of $R^2=0.999$. Our precise quench-rate for the glass preparation is unknown, but is expected to conform to the range of 100–1000 K/s.^{S4,S5} Extrapolation of the data in Fig. S1(d) to these limiting values resulted in the predictions of $T_f=933$ K (660 °C) and $T_f=973$ K (700 °C) at $q_c=100$ K/s and $q_c=1000$ K/s, respectively. They may be compared with the experimentally determined T_g -value of 1149 K (876 °C).^{S6} Whereas experimental values of T_g and T_f are only approximately equal, by assuming that $T_g^{exp} \approx T_f^{exp}$, we conclude that the extrapolation of the simulated data reproduced the experimental value within $\approx 20\%$. The modeled fictive temperatures span ≈ 700 K across the range of cooling rates relevant for the modeled (10^{13} K/s) and laboratory-prepared (10^3 K/s) glass structures. Further, if assuming that the simulated result $T_f=1680$ K is devoid of (large) systematic errors and that the underestimation of the T_g -value at $q_c = 10^3$ K/s originates entirely from the data-extrapolation over ten orders of magnitude, the difference between experimental and modeled results reduces slightly to $\Delta T_f = T_f^{sim} - T_f^{exp}=531$ K.



Figure S1. (a) MD-derived molar configurational energy plotted against temperature for the $La_{0.59}^{0.33}(2.54)$ glass and quench-rate $q_c=1$ K/ps. The fictive temperature is obtained as the intersection between the two straight lines extrapolated from low temperatures in the glass (blue line) and high temperatures in the melt (red line). (b) As in (a), but plotted over a larger (E, T)-range and showing results from four distinct cooling rates. Each curve is identified with its respective q_c -value in (c) that displays a zoom over the low-temperature region. (d) Logarithm of the quench-rate plotted against the inverse fictive temperatures provided the estimated $T_{\rm f}$ -values of 973 K and 933 K at $q_c=1000$ K/s and $q_c=100$ K/s, respectively, *i.e.*, the upper and lower limits representative for our water-quenched glass specimens. The uncertainty in $T_{\rm f}$ is ± 30 K, which is marginally larger than the symbol sizes in (d).



Figure S2. Experimental ²⁷Al MAS NMR spectra (black traces) from the as-indicated La AS glasses recorded at 14.1 T (left panel) and 9.4 T (right panel), shown together with deconvolutions into three component peaks (gray traces) stemming from each ²⁷Al^[p] (p=4, 5, 6) coordination. The curve beneath each NMR spectrum represents the difference between experiment and best-fit. Spinning sidebands are marked by asterisks. See Table S2 for the corresponding best-fit data and results from additional samples.



Figure S3. Radial distribution functions (RDFs) for Si–O, Al–O and La–O (left panel), and Si–Si, Al–Al and La–La (right panel), plotted for La AS glasses associated with $r\approx 2.21$ and the $n_{\rm Al}/n_{\rm Si}$ ratio equal to 0.30 (black traces), 0.65 (red) and 1.17 (green).

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Figure S4. Bond-angle (θ) distribution for the as-indicated X-Y-Z structural fragments and La(2.21) glasses with $n_{\rm Al}/n_{\rm Si}$ equal to 0.30 (black traces), 0.65 (red) and 1.17 (green). Note the widened X-O-Y angles along the series θ (Al-O-Al) $<\theta$ (Si-O-Al) $<\theta$ (Si-O-Si). The θ (Al-O-Al) values $\approx 90^{\circ}$ stem from edge-shared polyhedra.

Quench		La coordinations ^b				Al coordinations				O coordinations			$x(T_1 - O^{[2]} - T_2)$			
rate	$T_{\rm f}$ (K)	\overline{Z}_{La}	$x_{\mathrm{La}}^{[5]}$	$x_{\mathrm{La}}^{[6]}$	$x_{\mathrm{La}}^{[7]}$	$x_{\mathrm{La}}^{[8]}$	\overline{Z}_{Al}	$x_{\mathrm{Al}}^{[4]}$	$x_{\mathrm{Al}}^{[5]}$	$x_{\mathrm{Al}}^{[6]}$	$x_{\rm O}^{[1]}$	$x_{\mathrm{O}}^{[2]}$	$x_{\mathrm{O}}^{[3]}$	Si–Si	$Si-Al^{[4]}$	$Al^{[4]} - Al^{[4]}$
$La_{0.63}^{1.03}(2.21)$																
$20 \mathrm{K/ps}$	1508	6.37	0.136	0.424	0.345	0.081	4.14	0.870	0.124	0.006	0.227	0.680	0.084	0.269	0.544	0.187
$10 \mathrm{~K/ps}$	1509	6.41	0.128	0.421	0.340	0.094	4.12	0.878	0.118	0.004	0.229	0.678	0.084	0.259	0.561	0.179
$10 \mathrm{K/ps^{c}}$	1526	6.39	0.129	0.435	0.336	$6 \ 0.085$	4.13	0.872	0.123	0.005	0.230	0.676	0.085	0.265	0.551	0.184
$5 \mathrm{K/ps}$	1477	6.42	0.125	0.419	0.354	0.089	4.13	0.875	0.118	0.007	0.227	0.678	0.085	0.259	0.552	0.189
$1 \mathrm{K/ps}$	1396	6.45	0.119	0.405	0.367	0.098	4.12	0.889	0.104	0.007	0.233	0.676	0.083	0.254	0.552	0.195
$La_{0.59}^{0.33}(2.54)$																
$20 \mathrm{~K/ps}$	1720	6.33	0.150	0.447	0.315	0.077	4.11	0.896	0.100	0.004	0.379	0.582	0.015	0.540	0.413	0.046
$10 \mathrm{~K/ps}$	1680	6.34	0.141	0.452	0.320	0.075	4.13	0.874	0.117	0.009	0.387	0.574	0.018	0.555	0.397	0.047
$10 \mathrm{K/ps^{c}}$	1669	6.35	0.137	0.446	0.325	5 0.078	4.11	0.893	0.101	0.006	0.384	0.578	0.016	0.549	0.402	0.049
$5 \mathrm{K/ps}$	1648	6.32	0.139	0.462	0.316	0.069	4.12	0.890	0.104	0.006	0.388	0.573	0.018	0.549	0.403	0.048
$1 \mathrm{K/ps}$	1567	6.36	0.142	0.430	0.337	0.080	4.11	0.898	0.096	0.006	0.384	0.581	0.014	0.546	0.404	0.050

^a Results of fictive temperatures, mean coordination numbers (\overline{Z}_{La} , \overline{Z}_{Al}) and fractional populations $x_E^{[p]}$ when employing a smaller system (~3500 atoms) for the La^{1.03}_{0.63}(2.21) and La^{0.33}_{0.59}(2.54) samples, and using variable cooling rates between 1 K/ps to 20 K/ps. The rightmost columns compare the fractional populatons of the $T_1O_4-T_2O_4$ contacts observed in each network. Except for a minor systematic increase in \overline{Z}_{La} as the quench-rate decreases in the case of the La^{1.03}_{0.63}(2.21) glass, no significant differences are observed among the modeled data-sets, all of which agree within their statistical uncertainties.

^b Only the most populated coordinations are displayed, with the remaining corresponding to minor contributions from $x_{\text{La}}^{[4]}$ and $x_{\text{La}}^{[9]}$.

^c Bold-face numbers are the results of Table 2, which were obtained by using 10 000 atoms and a quench rate of 10 K/ps.

	Isotropic c	chemical shif	ts (ppm)	Quadrupo	lar produc	cts (MHz)	Fractional populations				
Glass	$\delta_{iso}^{[4]}$	$\delta_{iso}^{[5]}$	$\delta_{ m iso}^{[6]}$	$C^{[4]}_{\mathbf{Q}\eta}$	$C_{\mathrm{Q}\eta}^{[5]}$	$C_{\mathrm{Q}\eta}^{[6]}$	$x_{ m Al}^{[4]}$	$x_{ m Al}^{[5]}$	$x_{ m Al}^{[6]}$		
La ^{0.30} _{0.28} (2.21)	61.0(61.0)	34.5(34.9)	7.5(7.6)	9.9(10.0)	8.1(8.1)	7.3(7.3)	0.910(0.949)	0.067(0.046)	0.023(0.005)		
$\operatorname{La}_{0.63}^{1.03}(2.21)$	66.6(66.7)	35.7(35.2)	7.1(7.1)	9.9(9.9)	8.1(8.2)	7.3(7.3)	0.879(0.887)	0.100(0.091)	0.021(0.022)		
$La_{0.72}^{0.71}(2.42)$	65.7(65.6)	33.9(33.1)	7.1(7.0)	9.8(9.8)	8.1(8.1)	7.3(7.3)	0.902(0.904)	0.081(0.073)	0.017(0.023)		
$\operatorname{La}_{1.02}^{1.18}(2.43)$	70.6(70.4)	35.6(35.4)	7.1(7.0)	9.8(9.8)	8.1(8.1)	7.3(7.3)	0.871(0.887)	0.099(0.087)	0.030(0.026)		
T ₀ 0.33(9 54)	62 8 (62 0)	22 0(22 2)	76(72)	0.6(0.6)	91(91)	79(79)	0.014(0.018)	0.064(0.050)	0.000(0.002)		
$La_{0.59}(2.04)$	03.8(03.9)	33.0(32.2)	1.0(1.3)	9.0(9.0)	0.1(0.1)	1.3(1.3)	0.914(0.918)	0.004(0.059)	0.022(0.023)		
La _{1.22} ^{1.21} (2.55)	71.3(71.4)	37.5(37.0)	8.5(7.4)	9.7(9.7)	8.1(8.2)	7.3(7.3)	0.870(0.870)	0.098(0.100)	0.032(0.030)		

Table S2: Deconvolution Results of 27 Al MAS NMR Spectra Recorded at $B_0=9.4$ T ^a

^a Best-fit results from deconvoluting a selected set of 27 Al MAS NMR spectra recorded at 9.4 T. The corresponding data displayed within parenthesis were obtained at 14.1 T and are reproduced from Table 2.

 $^{8}_{S}$

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