Structural Origins of Crack Resistance on Magnesium Aluminoborosilicate Glasses Studied by Solid State NMR

Henrik Bradtmüller,[a] Tobias Uesbeck,[a] Hellmut Eckert,[a,b*]

[a]Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 30, D-48149 Münster, Germany.

[b]Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13566-590, São Carlos, SP, Brasil.

Tetsuya Murata,[c] Shingo Nakane,[c] Hiroki Yamazaki[c]

[c]Nippon Electric Glass, Otsu Japan, 7-1, Seiran 2-chome, Otsu, Shiga 520-8639, Japan.

*corresponding author. Email eckrth@uni-muenster.de

Supporting Materials Section

Description of the Double Resonance Methodology.

The experimental strategy employed in the present study includes the quantitative analysis of high-resolution ^{11}B, ^{29}Si, ^{23}Na, and ^{27}Al MAS-NMR spectra in conjunction with a quantitative analysis of their internuclear magnetic dipole-dipole interactions. Figure S1 shows the $S\{I\}$ REDOR and REAPDOR pulse sequences used in the present study.[1-3] A normalized difference signal $\Delta S/S_0 = (S_0\text{-}S)/S_0$ is measured in the absence (intensity S_0) and the presence (intensity S) of the dipolar interactions between the observed nuclei S and the second nuclear species I.

Determination of $\Delta S/S_0$ under systematic variation of the number of rotor cycles N yields the so-called REDOR curve, in which the data are plotted as a function of dipolar evolution time NT_r (T_r being the duration of one rotor period). For isolated spin-1/2 pairs these curves possess a universal shape, allowing straightforward determination of the magnetic dipole-dipole coupling constant. In contrast, the analysis of $S\{I\}$ REDOR curves in inorganic glasses is complicated by multispin interactions, distance distributions and interference by nuclear electric quadrupolar couplings. We have previously shown that in the case of $S\{I\}$ REDOR experiments with I = 1/2 nuclei, the problem can be simplified by confining the REDOR data analysis to the initial curvature, where $\Delta S/S_0 \leq 0.2$.[4,5] In this limit the REDOR curve is found to be independent of specific spin system geometries, and can be approximated by a simple parabola:

$$\frac{\Delta S}{S_0} = \frac{4}{3\pi^2} M_2^{SI} \left(NT_r\right)^2 \qquad (1)$$

From the curvature of this parabola we can determine the van-Vleck second moment[6] $M_{2(S\text{-}I)}$, a quantity that can be used to characterize the average dipole-dipole coupling strengths the S nuclei experience from the magnetic moments of their neighboring I nuclei. The approach yields satisfactory results also in amorphous and strongly disordered systems where the order and geometry of the spin systems is unknown and possibly ill-defined. This experimental M_2 value can then be compared with calculations based on structural models using the well-known van Vleck equation:[6]

$$M_{2(S-I)} = \frac{4}{15}\left(\frac{\mu_0}{4\pi}\right)^2 I(I+1)\gamma_I^2\gamma_S^2\hbar^2 N^{-1} \sum_I \frac{1}{r_{SI}^6}. \qquad (2)$$

where γ_I and γ_S are the gyromagnetic ratios of the nuclei I and S involved, and r_{IS} are the internuclear distances.

In those cases, where the dipolar dephasing of the observed spins occurs in the local field of $I > 1/2$ nuclei such as ^{23}Na ($I = 3/2$) several additional complications enter. First of all, the different possible Zeeman states m_I for the I nuclei differ in the respective sizes of their z components and hence generate dipolar fields of different magnitudes at the observed spins. Secondly, for strong nuclear electric quadrupolar coupling, the anisotropic broadening of the $|1/2\rangle \leftrightarrow |3/2\rangle$ "satellite transitions" produces large resonance offsets, which reduce the efficiency of π pulses in causing population inversion. In the limit of very large first-order quadrupolar splitting (rf nutation frequency $\nu_1 << C_Q$, the quadrupolar coupling constant), pulses applied to the I nuclei in the REDOR sequences will affect only the central $|1/2\rangle \leftrightarrow |-1/2\rangle$ coherences. In this regime only those S spins that are coupled to I nuclei in Zeeman states with $|m_I| = 1/2$ are expected to yield a REDOR response. In this case the above approach can still be used if the results are calibrated by parallel measurements on a crystalline model compound having similar spin dynamics as the samples under investigation. Alternatively, the REAPDOR method[8] (Figure S1c) can be used. In this sequence, the dipolar recoupling pulses are placed on the channel of the observe-nuclei, while the adiabatic passage through the various Zeeman transitions of the non-observed quadrupolar nuclei I are swept through during the MAS rotation, while a continuous – wave pulse is applied for 1/3 of the rotor period. The extent of dipolar recoupling depends on both the strength of the quadrupolar interaction, the spinning speed and the amplitude of the radio frequency field applied, as measured by nutation frequency of the quadrupolar nuclei. In defining the nutation frequency one typically one specifies the non-selective case valid in the liquid state. To extract dipolar coupling information, detailed simulations are necessary, which can be done using, for example the SIMPSON software.[9]

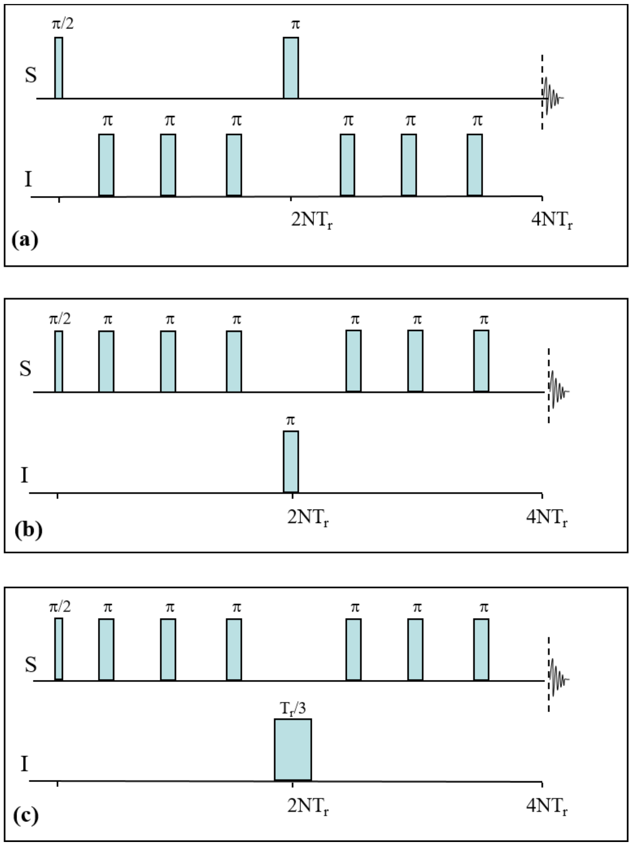


Figure S1: NMR pulse sequences used in the present study. *a)*: sequence used for S{I} REDOR, *I* = 1/2; *b)*: sequence used for S{I} REDOR, *I* = 3/2; *c)*: a related method, called Rotational Echo Adiabatic Passage Double Resonance (REAPDOR), in which a pulse of a duration of 1/3 of the rotor period is applied to the quadrupolar *I* nuclei.

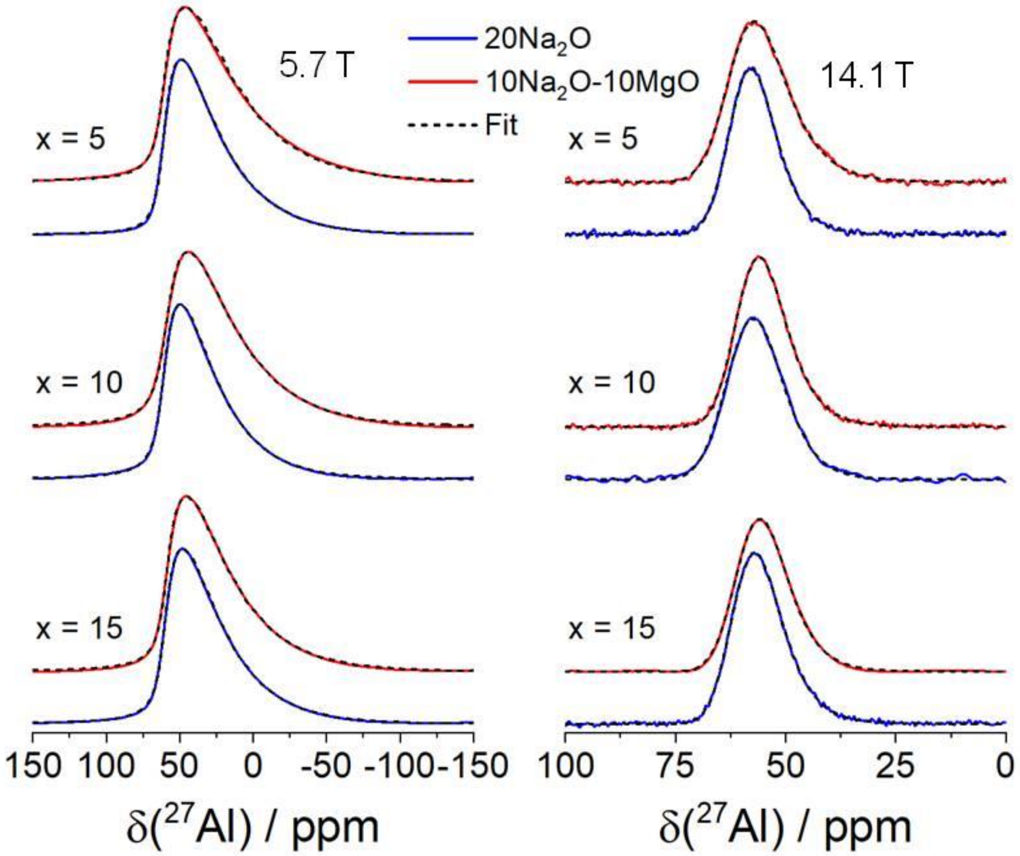


Figure S2: Field dependent ^{27}Al MAS-NMR spectra at of the glasses $60SiO_2$-(20-x)Al_2O_3-xB_2O_3 with $20Na_2O$ and $10Na_2O$-$10MgO$ as network modifier. Left: 5.7T, right: 14.T. Black dashed curves are Czjzek fits.

Table S1: Isotropic chemical shifts (± 1.0 ppm) and average quadrupole coupling constants C_Q (±0.5 MHz) from lineshape simulation with the Czjzek model measured at 14.1 T and 5.7 T.

Sample	δ_{iso} / ppm		Avg. C_Q / MHz	Avg. C_Q / MHz
$20Na_2O$	14.1 T	5.7 T	14.1 T	5.7 T
x = 5 / Al$^{(6)}$	61.9	62.3	4.2	4.3
x = 10 / Al$^{(4)}$	61.7	61.8	4.3	4.2
x = 15 / Al$^{(4)}$	61.2	61.4	4.3	4.1
$10Na_2O$-$10MgO$				
x = 5 / Al$^{(4)}$	62.4	62.5	5.0	4.7
x = 10 / Al$^{(4)}$	60.5	60.6	4.5	4.5
x = 15 / Al$^{(4)}$	60.2	60.2	4.5	4.3

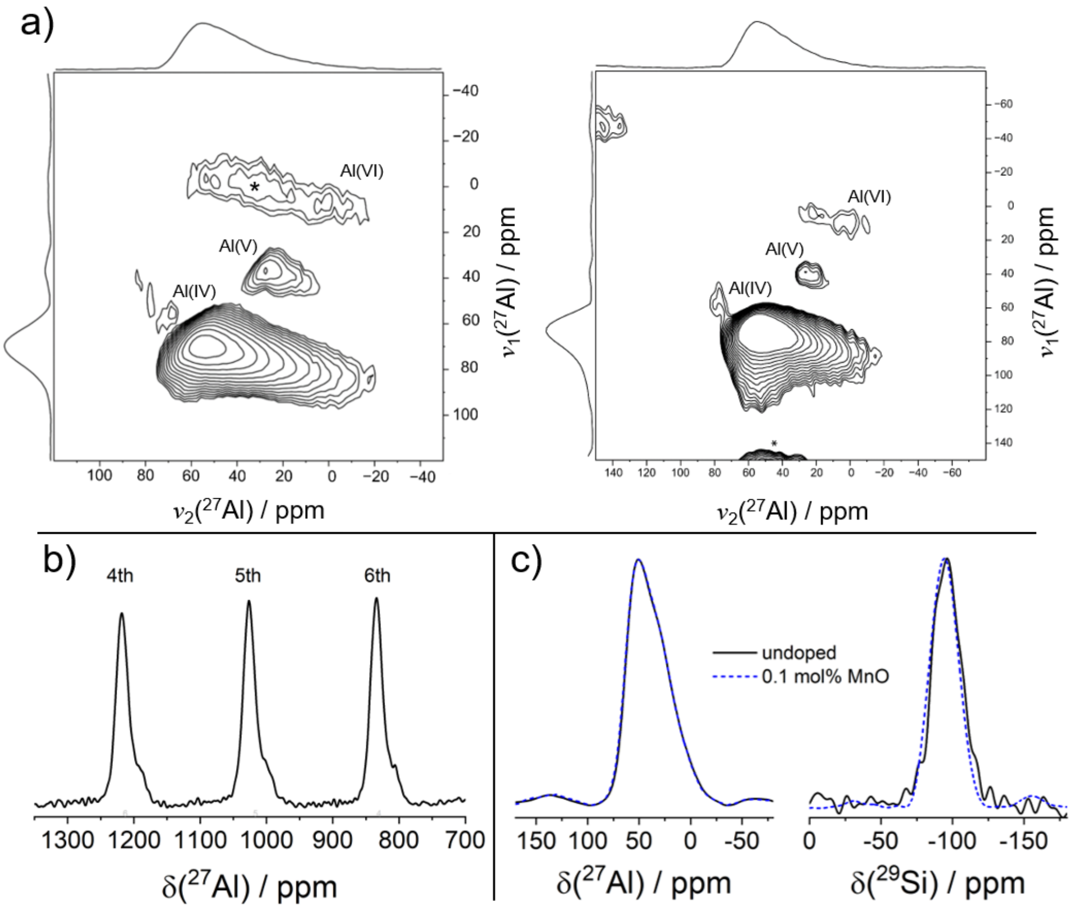


Figure S3: NMR studies of 60SiO$_2$-20Al$_2$O$_3$-20MgO glass in the undoped state and doped with 0.1 mol% MnO. *a)*: ^{27}Al TQMAS-NMR spectra of the undoped glass (left) and doped glass (right). Right: *b)*: Set of fourth, fifth and sixth ^{27}Al MAS-NMR spinning sidebands of the undoped glass. *c)*: ^{27}Al and ^{29}Si MAS NMR spectra.

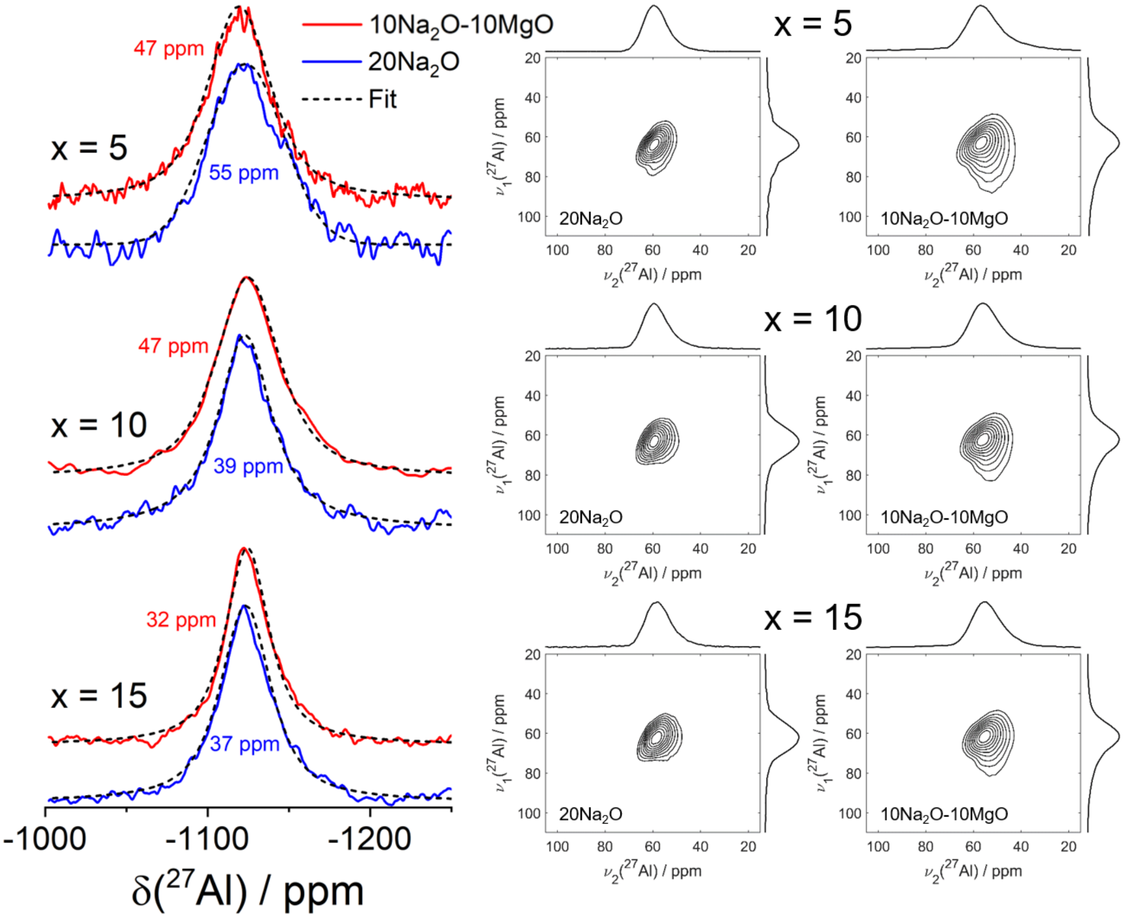


Figure S4: *Left*: ^{27}Al MAS-NMR spectra of the 5th order spinning sidebands at 5.7 T, which are dominated by the $|m|= ½ <-> |m| = 3/2$ Zeeman transitions. These spectra are not influenced by second-order quadrupolar effects. The comparable linewidths of the Na and Na-Mg containing glasses indicate that the linebroadening observed in the central transition spectra (Figure 1 right) arise from quadrupolar interactions accounted for by second-order perturbation theory and not from isotropic chemical shift distributions. *Right*: ^{27}Al 14.1 T- TQMAS-NMR spectra of glasses with the compositions: $60SiO_2$-(20-x)Al_2O_3-$x$$B_2O_3-20Na_2O$ and $60SiO_2$-(20-x)Al_2O_3-$x$$B_2O_3-10Na_2O$-10MgO. All of these data reveal the absence of higher-cordinated Al units for glasses with $x \neq 0$.

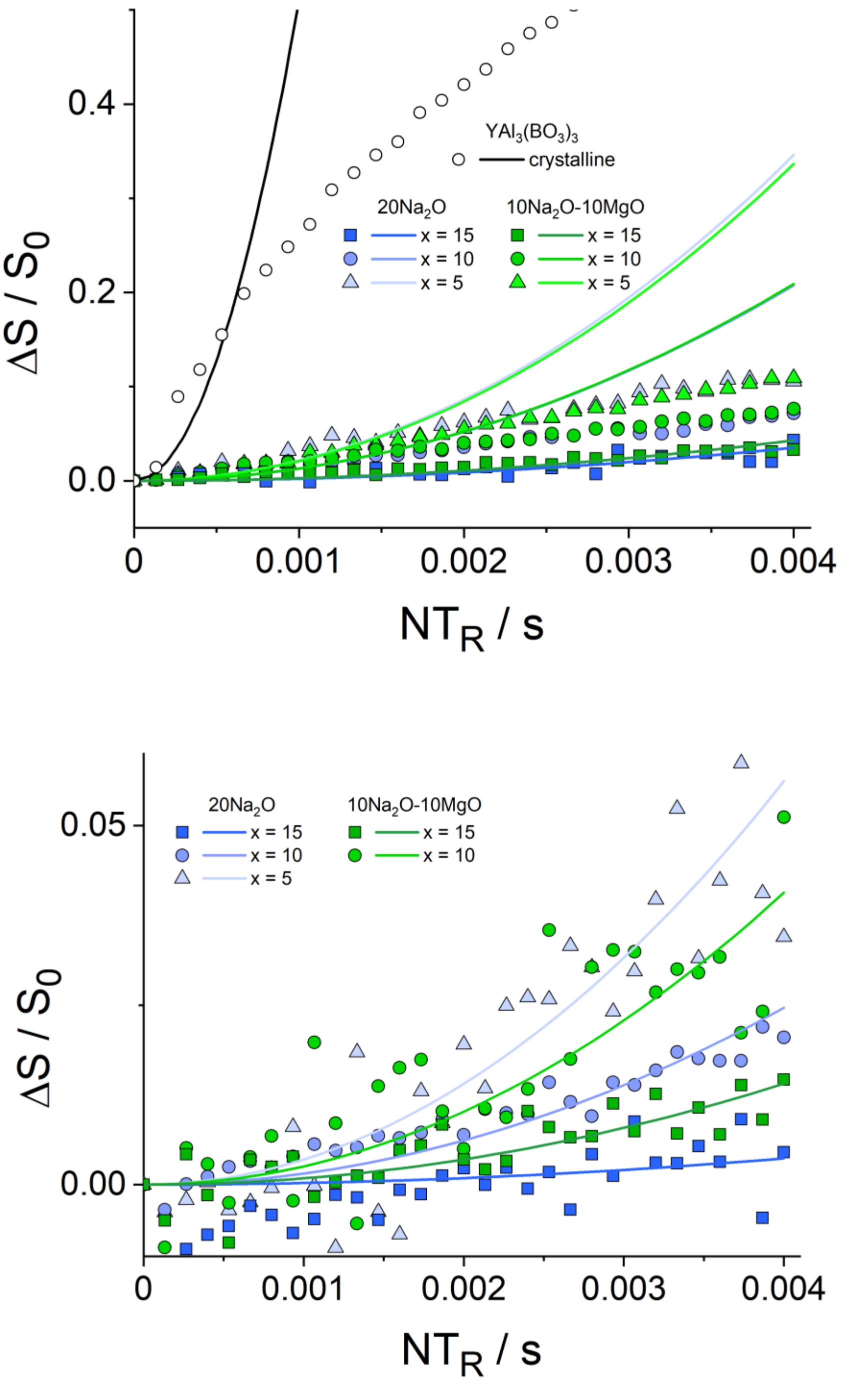


Figure S5: *Top*: Comparison of the ^{11}B{^{27}Al} REDOR data for the B$^{(3)}$ units of the glasses with those measured for the model compound YAl$_3$(BO$_3$)$_4$. *Bottom*: B$^{(4)}$ observed ^{11}B{^{27}Al} REDOR data. The dipolar interactions strengths are found to be very low.

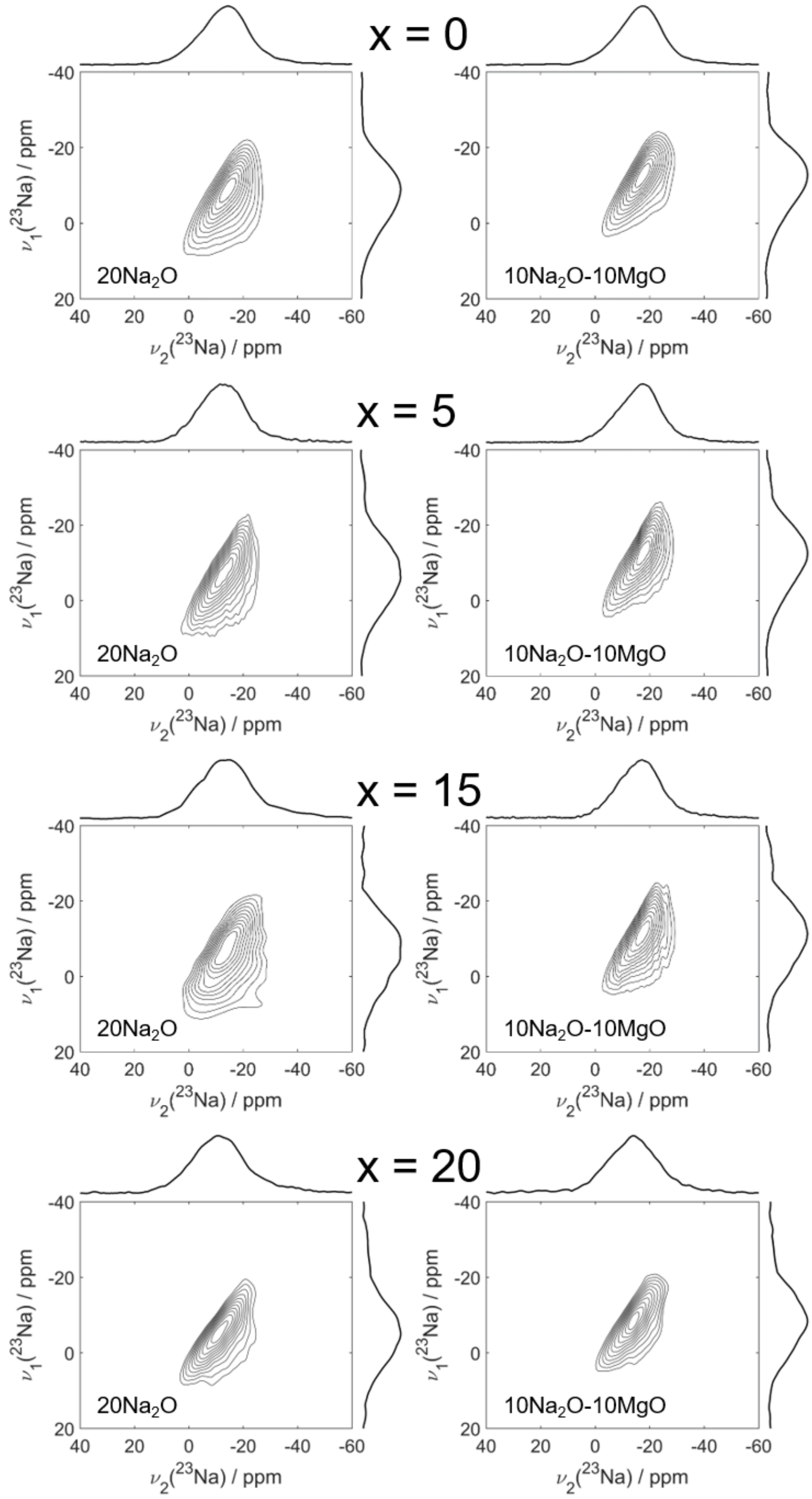
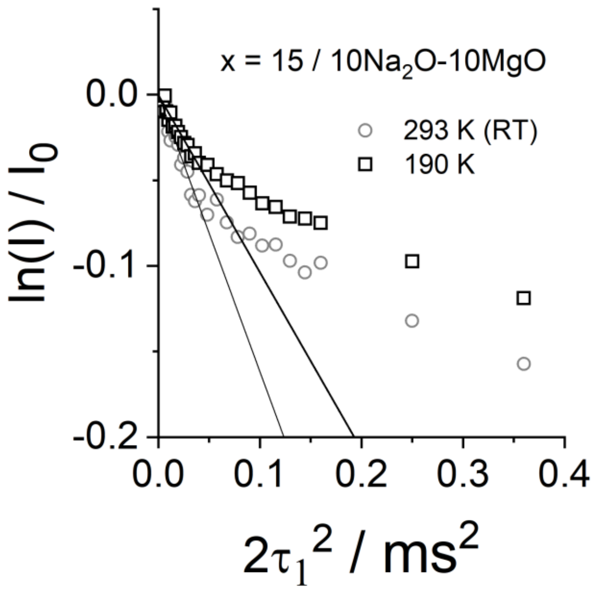
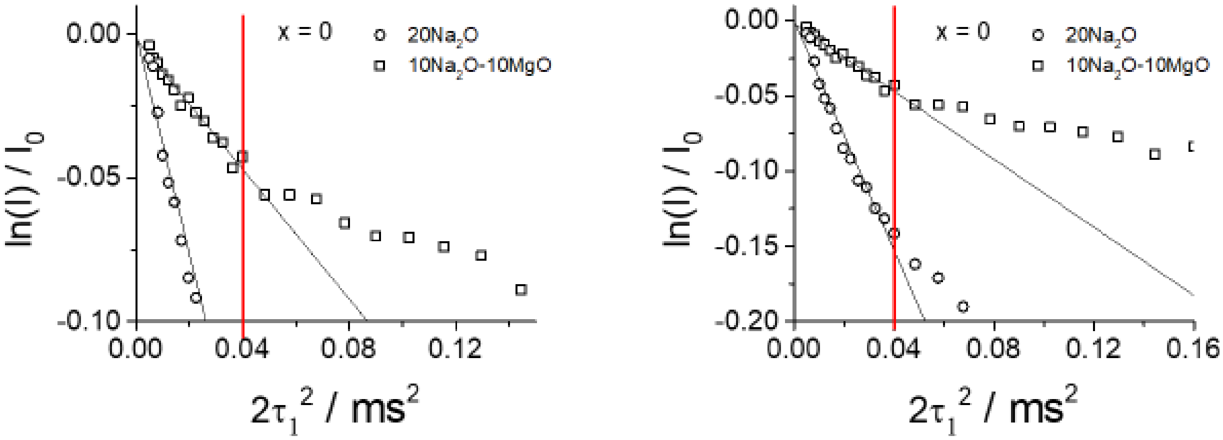


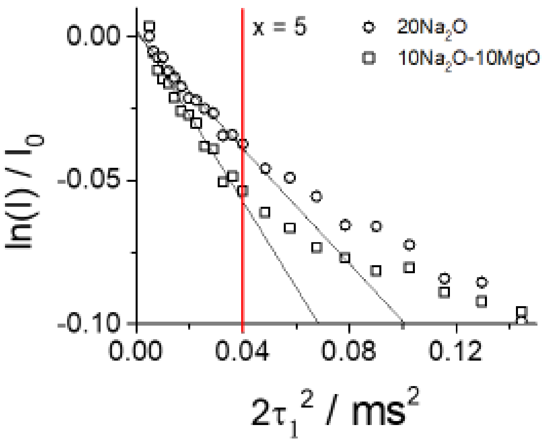
Figure S6: ^{23}Na TQMAS data recorded at 11.7 T on $60SiO_2$-(20-*x*)Al_2O_3-*x*B_2O_3 glasses with single $20Na_2O$ (right) and mixed $10Na_2O$-10MgO network modifier content (left).

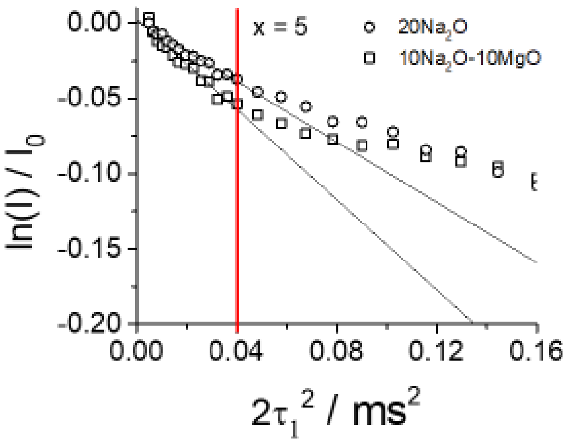
a)

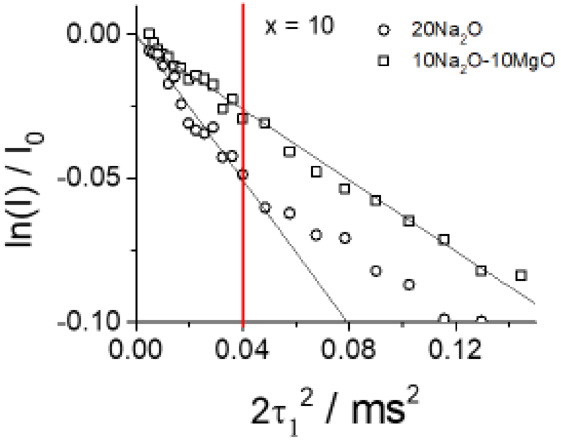

x = 15 / 10Na$_2$O-10MgO
293 K (RT)
190 K
ln(I) / I$_0$
0.0
-0.1
-0.2
0.0
0.1
0.2
0.3
0.4
2τ$_1$^{2} / ms^2

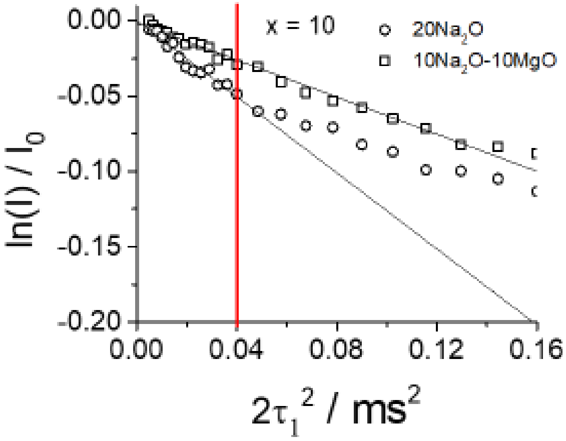
b)


x = 0
20Na$_2$O
10Na$_2$O-10MgO
ln(I) / I$_0$
0.00
-0.05
-0.10
0.00
0.04
0.08
0.12
2τ$_1$^{2} / ms^2
x = 0
20Na$_2$O
10Na$_2$O-10MgO
ln(I) / I$_0$
0.00
-0.05
-0.10
-0.15
-0.20
0.00
0.04
0.08
0.12
0.16
2τ$_1$^{2} / ms^2


x = 5
20Na$_2$O
10Na$_2$O-10MgO
ln(I) / I$_0$
0.00
-0.05
-0.10
0.00
0.04
0.08
0.12
2τ$_1$^{2} / ms^2


x = 5
20Na$_2$O
10Na$_2$O-10MgO
ln(I) / I$_0$
0.00
-0.05
-0.10
-0.15
-0.20
0.00
0.04
0.08
0.12
0.16
2τ$_1$^{2} / ms^2


x = 10
20Na$_2$O
10Na$_2$O-10MgO
ln(I) / I$_0$
0.00
-0.05
-0.10
0.00
0.04
0.08
0.12
2τ$_1$^{2} / ms^2


x = 10
20Na$_2$O
10Na$_2$O-10MgO
ln(I) / I$_0$
0.00
-0.05
-0.10
-0.15
-0.20
0.00
0.04
0.08
0.12
0.16
2τ$_1$^{2} / ms^2

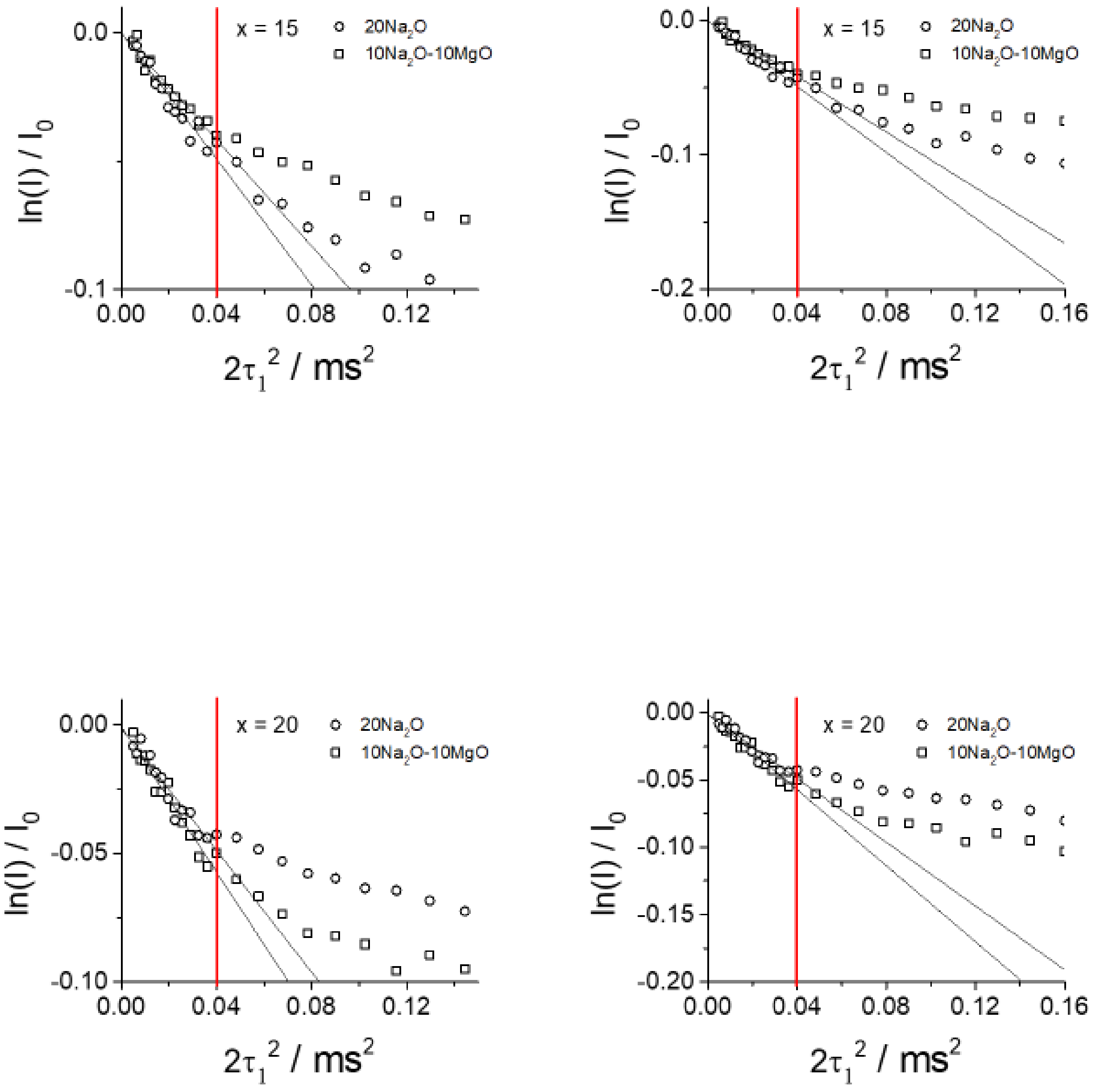


Figure S7: a) Static ^{23}Na spin echo decay experiments on glass with composition *x* = 15 at room temperature (RT) (gray circles) and at 190 K (squares). The more rapid decay observed at room temperatures indicates a dynamic contribution to ^{23}Na spin relaxation. b) expanded views of the ^{23}Na spin echo decay data. Red vertical lines indicate the data range used for the analysis. Black solid lines indicate semilogarithmic fits of the data to eq. (3).

References

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