The structural role of water in silicate glasses: ^{1}H and ^{29}Si NMR evidence

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1 Introduction

Over the last years various spectroscopic methods [1-6] have been used to investigate hydrous silicate and aluminosilicate glasses and to clarify the structural role of water in such systems. Especially, the existence of molecular water and/or Si-OH/Al-OH species, i.e. the H_2O-induced depolymerisation of the Si/Al or Si network in such glasses has been discussed controversially in the literature.

We have chosen two hydrous $Na_2Si_4O_9$ glasses with different H_2O-contents as an Al-free model system.

The Al-free $Na_2Si_4O_9$ system is particularly well suited for high-resolution solid-state NMR investigations as the various Q-species can easily be resolved in the respective ^{29}Si MAS and CP/MAS spectra.

Various high resolution solid state NMR techniques were used: ^{29}Si single pulse MAS, ^{1}H → ^{29}Si-CP/MAS and ^{1}H-CRAMPS. Only the combined use of all these methods provides an insight into the interactions between the Si-network and the proton system. Additional modifications of these standard techniques were then used to confirm and to refine the picture of the $Na_2Si_4O_9/H_2O$ system. The new results presented here are based on preliminary investigations published elsewhere [7].

2 Experimental

Two hydrous $Na_2Si_4O_9$ glasses, "$Na_2Si_4O_9$ 10% H_2O" and "$Na_2Si_4O_9$ 5% H_2O" (water content analysed by Karl-Fischer-Titration of 9.1% and 4.8%, respectively) were investigated. The preparation of these samples is described in [7].

All NMR spectra were recorded on a BRUKER MSL 300 spectrometer equipped with a standard 7 mm double bearing probe (for ^{29}Si-CP/MAS measurements at 58.6 MHz) and a ^{1}H-CRAMPS probe operating at 300.1 MHz.

^{29}Si-CP/MAS spectra were run with a ^{1}H-90° pulse of 5 μs, a recycle delay of 5s and 4.0 kHz MAS frequency. For an unambiguous deconvolution of the spectra 4000 transients were accumulated to obtain an excellent signal-to-noise ratio.

The ^{29}Si-CP/MAS experiment with interrupted decoupling as proposed by Opella and Frey [8] was modified by π pulses both in the proton and the ^{29}Si channel at half the dephasing time [9] in order to avoid phase distortions.

To obtain resolved ^{1}H spectra, the MREV8 pulse sequence [10] was used. The spectra were recorded with a ^{1}H-90° pulse of 2.0 μs and a cycle time of 45.6 μs. The MAS frequency of 3.5 MHz was chosen to avoid any interference between sample rotation and the pulse sequence. Additional modifications as proposed by Bronnimann et al. [11] were used to measure T_1

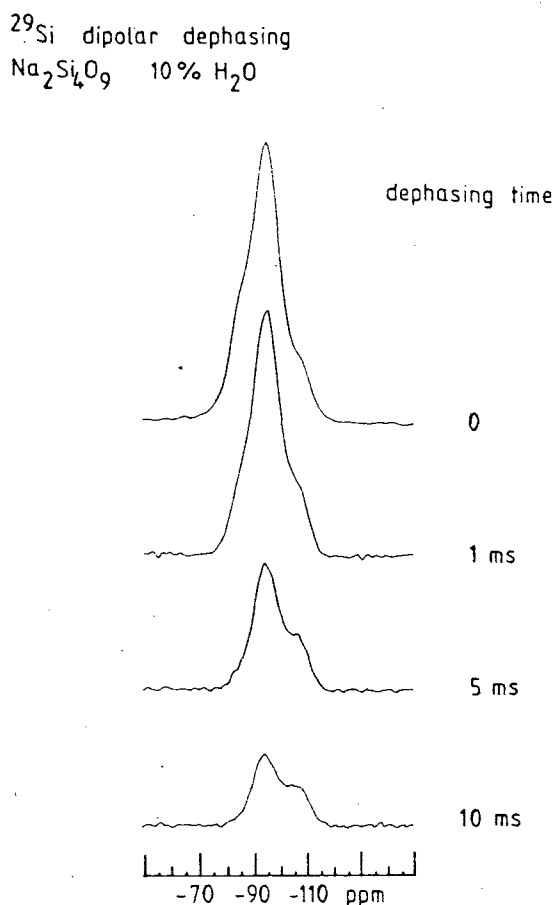selectively and to obtain separate information about the dipolar proton-interactions ("dipolar dephasing").

^{29}Si dipolar dephasing
$Na_2Si_4O_9$ 10% H_2O

dephasing time

0

1 ms

5 ms

10 ms

-70 -90 -110 ppm

Fig. 1: ^{29}Si-CP/MAS dipolar dephasing spectra of $Na_2Si_4O_9$ glass with 9.1% H_2O. The glass with the lower water content shows similar decays of the signal components.

3 Results and Discussion

The ^{29}Si-MAS and ^{29}Si-CP/MAS spectra of the hydrous glasses show the presence of Q_4, Q_3 and Q_2 silicon species. The higher water content corresponds to a higher relative intensity of the Q_2 signal and to a

lower relative intensity of the Q_4 signal, respectively. Furthermore, the ^{29}Si-CP/MAS experiments show significant differences in the time dependence of the ^{29}Si magnetization of the two glasses. For the glass with the higher water content the signal intensity as a function of contact time is describable by a biexponential curve according to the usual thermodynamic model used to describe I-S CP-dynamics. The cross polarization times T_{IS} and the relaxation times $T_{1\rho}$ show a trend for $(Q_4) > (Q_3) > (Q_2)$. Both T_{IS} and $T_{1\rho}$ are significantly longer for the glass with the lower water content. The ^{29}Si CP-data of the Q_3 and Q_4 species for the lower H_2O-content material can only be described by double-biexponential magnetization curves. This leads to the following conclusions: i) in the glass with the higher water content a uniform ^1H spin lattice is established, ii) due to the dilution of the protons in the other glass at least two ^1H spin baths are present and iii) in the lower H_2O-content glass the average interatomic distances between ^{29}Si and ^1H for the two different reservoirs must be significantly different. In consequence, one can assume the presence of both Si-OH groups and molecular water in these hydrous glasses. In fact, quantitative determination of the Q_2, Q_3 and Q_4 species in both hydrous glasses from ^{29}Si MAS spectra and comparison of these results with the respective stoichiometric requirements if fully in accord with the depolymerisation of the silicate network.

Results of the ^{29}Si-CP/MAS experiment with interrupted decoupling ("dipolar dephasing") are illustrated in Fig. 1. The decay of the ^{29}Si magnetization is mainly determined by the strength of the dipolar interaction between the ^{29}Si nuclei and the nearest surrounding proton system. Obviously, for the loss of magnetization characterized by a decay time T_2 the relation $T_2(Q_2)<T_2(Q_3)<T_2(Q_4)$ is valid, i.e., the Q_2 species are affected by the strongest dipolar ^1H-^{29}Si interaction. Therefore, neglecting effects of spin diffusion and molecular motion, the Q_3 and Q_2 signals can be assigned to silicons attached to one or two OH-groups, respectively.
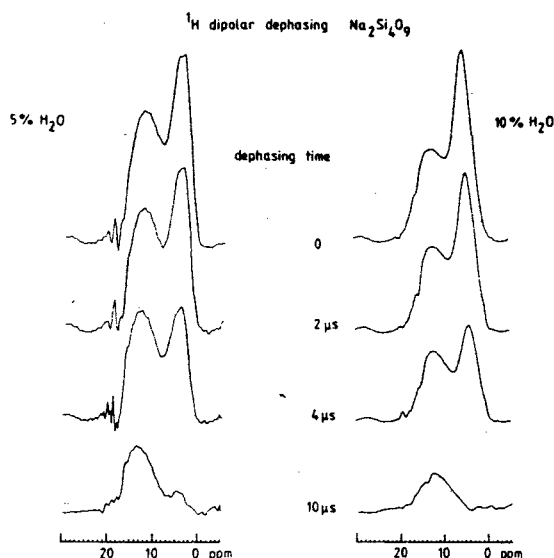
Fig. 2: ^{1}H-dipolar dephasing CRAMPS spectra of both glasses (450 scans). (The spectra on the left hand side show an experimental artefact at ca. 18ppm)

To confirm these CP results various ^{1}H multiple pulse experiments were used. The ^{1}H-CRAMPS spectra clearly show two well resolved signals at ca. 4.7 ppm and 12.2 ppm (with respect to TMS = 0.0 ppm). The chemical shifts and the results of the CP experiments allow tentative assignment of these signals as molecular water (4.7 ppm) and protons of Si-OH groups (12.2 ppm). This assignment was confirmed by the ^{1}H "dipolar dephasing" CRAMPS experiment ($\pi/2-\tau-\pi-\tau-$MREV8). As illustrated in Fig. 2, in both glasses the signal at 4.7 ppm decays much faster than the less shielded signal, i.e., the dipolar ^{1}H - ^{1}H interaction is significantly stronger. This experimental fact corroborates the model proposed above. Comparing the decay rates found for the two different glasses, differences in these rates were found (Fig. 3). Again, these differences are in good agreement with the results of the standard ^{29}Si-CP/MAS experiments.
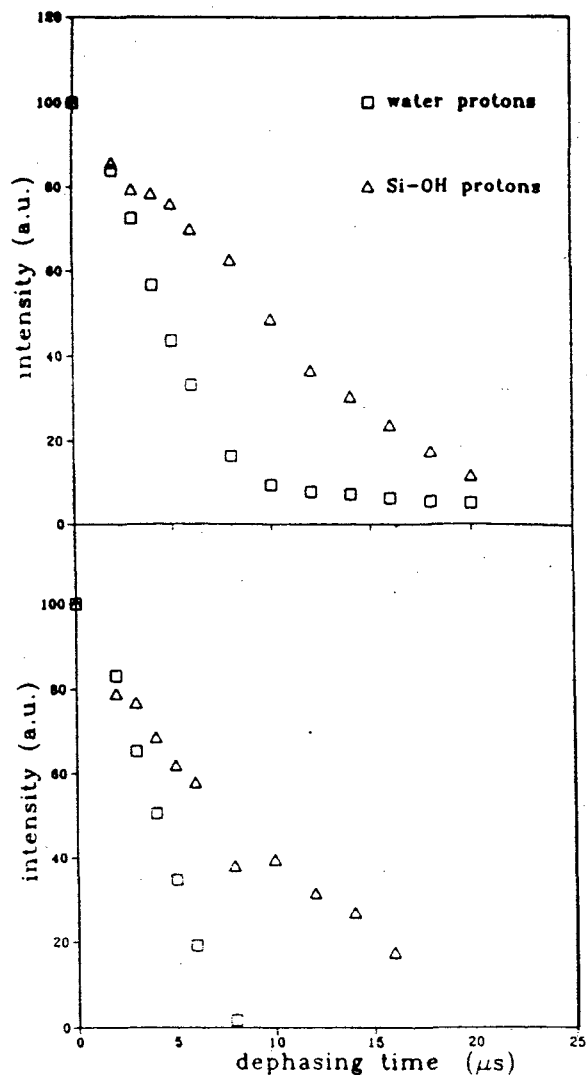

Fig. 3:   Signal intensities in the ^{1}H dipolar dephasing CRAMPS experiment for the $Na_2Si_4O_9$ glass with
a) 4.9 % H_2O (top)
b) 9.1 % H_2O (below)

Additionally, the longitudinal relaxation times T_1 of both ^{1}H signal components in both glasses were measured. The use of a $\pi-\tau-\pi/2-\tau-$MREV8 pulse sequence provides a uniform T_1 of 0.70 ± 0.05 s for the glass with the higher water content. In contrast, the signal components of the other glass decay with T_1(SiOH) = 0.85 ± 0.05 s and T_1(H_2O) = 0.97 ± 0.05 s, respectively. These data also confirm the interpretation of the CP experiments and provide an additional support for the following conclusions:

(1) H_2O does depolymerize the silicate network,

(2) both Si-OH and molecular water are present, and

(3) in the lower H_2O-content glass the more dilute proton system, forming these components is best described as "separate" sub-systems.

To answer further questions concerning the interactions between Si-OH and H_2O protons and to address questions concerning the structural role of cations like e.g. Na^+ in such silicate networks, 1D and 2D-spin diffusion experiments are in preparation.

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