Hydration in Alkali-silicate Glasses Studied by Two Dimensional Multi-Quantum Magic Angle Spinning

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The hydration in Na_2O-$3SiO_2$ glass was studied by ^{23}Na Magic Angle Spinning (MAS) and 2D MQMAS NMR spectroscopy. It was found that one-dimensional MAS spectra for the hydrated glasses with more than 8.4 wt% water consist of two signals at around –10 and –40 ppm. On the other hand, anhydrous glass and glass with low water content (2.8 wt%) give a single resonance line at around –10 ppm. From 2D MQMAS spectra, the isotropic chemical shift (δ_{iso}) and the quadrupole coupling frequency (ν_Q) for two sites (Na(1) and Na(2)) were estimated: δ_{iso} = 4.2 ppm and ν_Q = 0.6 MHz for Na(1) and δ_{iso} = 10.2 ppm and ν_Q = 1.3 MHz for Na(2). These results are discussed together with our previous results of ^{29}Si and ^{1}H NMR, and infrared spectra. It is speculated that Na(1) may exist in a similar environment as that in anhydrous sodium-silicate glasses, while Na(2) may be attached directly to water molecules.

Key words: Glass; Hydration; ^{23} Na; 2D MQMAS.

Introduction

It is well known that incorporation of water in vitreous silicates affects the physical and chemical properties of the glasses [1]. Much effort has been made to understand the mechanism of this process not only in the field of glass science but also in the field of geology. However, this mechanism is not well understood. Even the fundamental question whether the silicate glass network is depolymerized by water incorporation is still open.

NMR is a powerful method to investigate the structural change of glasses by their reaction with water, and therefore many works have already appeared. Zheng *et al.* [2] have concluded that depolymerization of the glass network occurs on the reaction of glass with water, and as a consequence Si-OH units are formed. Zotov and Keppler [3] measured ^{29}Si Magic Angle Spinning (MAS) NMR of hydrated glass and found breakage of the =Si-O-Si= linkage with water content. On the other hand, some authors insist that such depolymerization does not occur. Kohn *et al.* [4] proposed that Si-OH units are formed not from the depolymerization but from the ion-exchange process between Na^+ and H^+. Pandya *et al.* [5] investigated sodium-silicate glasses corroded by water for 6 years at low temperature. They found that the glasses contain high amounts of molecular water, but there is not any significant change in ^{29}Si MAS spectra, implying that there is not any significant depolymerization of the silicate network. In discussing the problem, it is very important to note that hydration does not proceed by a single reaction but by several different reactions. A typical model was proposed by Charles [6]. In that model, hydration of glass proceeds in three steps:

$$\equiv\text{Si-O-Na}^+ + H_2O \rightarrow \equiv\text{Si-OH} + \text{Na}^+ + \text{OH}^-, \quad (1)$$

$$\equiv\text{Si-O-Si}\equiv + \text{OH}^- \rightarrow \equiv\text{Si-OH} + \equiv\text{Si-O}^-, \quad (2)$$

$$\equiv\text{Si-O}^- + H_2O \rightarrow \equiv\text{Si-OH} + \text{OH}^-. \quad (3)$$

It can be seen that, once reaction (1) proceeds, the depolymerization takes place continuously by the repetition of (2) and (3). In addition to such reactions, the recombination

$$2\ \text{Si-OH} \rightarrow =\text{Si-O-Si}= + H_2O \quad (4)$$

may become important especially, when the concentration of Si-OH and H_2O becomes high [7]. Most researchers who insist on the absence of structural changes with hydration seem to use hydrated glasses with high water content (30wt%), while those stressing the decomposition examine glass with low water content (< 10wt%). It is a reasonable hypothesis that the different views on the structural changes arise because different stages of the reaction are observed. To clarify this point, we investigated hydrated sodium silicate glasses with a wide range of water content (0 to 30wt%) at low temperature (< 100 °C), using ^{29}Si, ^{1}H NMR and Infrared spectra [8]. We have shown that the glass network decomposes slightly at the initial stage of hydration, and that significant recombination of Si-OH occurs above 20wt% of water content. The result suggests that the above hypothesis may be correct. However, more information is necessary to discuss the hydration mechanism in this system. In particular, knowledge of the chemical state of sodium is of importance.

High speed ^{23}Na Magic Angle Spinning (MAS) NMR is helpful in obtaining information on the sodium environment, but recently two dimensional Multi-Quantum MAS (2D MQMAS) NMR [9] has proven to be more informative in elucidating the environment of quadrupolar nuclei. ^{27}Al [10 - 14], ^{11}B [15 - 17], ^{17}O [17 - 20], and ^{23}Na [10 - 12, 14, 21] MQMAS spectra have already been applied to study the structure of glasses.

In the present study, the hydration mechanism in sodium silicate glasses hydrated at low temperature is investigated using high resolution ^{23}Na NMR spectroscopy. ^{23}Na 2D MQMAS NMR as well as the conventional ^{23}Na MAS NMR is applied to examine the chemical state of sodium.

Experimental

Anhydrous glass of composition Na_2O-$3SiO_2$ was prepared by melting a stoichiometric mixture of Na_2CO_3 and SiO_2 at 1300 °C for 4 h in a Pt crucible. Hydrated glasses with various water contents were prepared by exposing the glass powder (125 - 250 µm) to saturated water vapor at 80 °C for different times. The weight gain during the hydration process was measured and used as the water content of the glass. Figure 1 shows the change of water content with the hydration time. The sample became totally gel-like after 6 h.

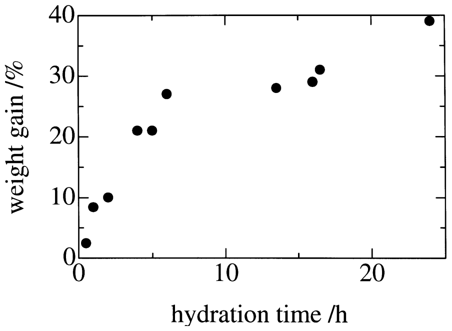

Fig. 1. Weight gain of powder Na_2O-$3SiO_2$ glass as a function of hydration time. The glass is hydrated at 80 °C in saturated water vapor.

All ^{23}Na MAS NMR spectra were measured on a Chemagnetics CMX-200 spectrometer with ν_0 = 52.9718 MHz (B_0 = 4.7 T). NaCl (1 M aq.) was used as a frequency reference. 1D MAS spectra were acquired using a single pulse of typically 1 µs with repetition time of 1 s. The spinning speed was set to 10 kHz. The signal was typically registrated 144 times.

To obtain 2D MQMAS spectra, the Z-filtering 3-pulse sequence and hypercomplex acquisition method was used to observe pure absorption spectra, following the procedure of Massiot *et al.* [22]. The lengths of the first and the second pulses and the amplitude of the third pulse were carefully optimized to maximize the signal without distortion. Typical pulse lengths were 4.2, 1.4, and 10 µs for the first, second, and third pulses, respectively. The delay time between the first and second pulse (dw_2) was set so as to $dw_2 = (1/4\nu_r)$, where ν_r is the sample rotation frequency [23]. Dwell times for t_1- and t_2-dimension were 25 and 9.7 µs, respectively. 384 or 768 transients of 256·48 data points were acquired. Zero-filling to 128 points in t_1-dimension and line-broadening of 200 Hz were employed. Proton decoupling [24] was not effective in enhancing the resolution of the MQMAS spectra.

Results

Figure 2 shows variation of ^{23}Na MAS NMR spectra in Na_2O-$3SiO_2$ glasses with hydration time. In the anhydrous sample an asymmetric absorption, the maximum of which is –10 ppm, is observed. This pattern is typical and often observed [4, 10, 25] for ^{23}Na in glasses. In the glasses with low water content (2.4wt%, Fig. 2(b)), no significant change was

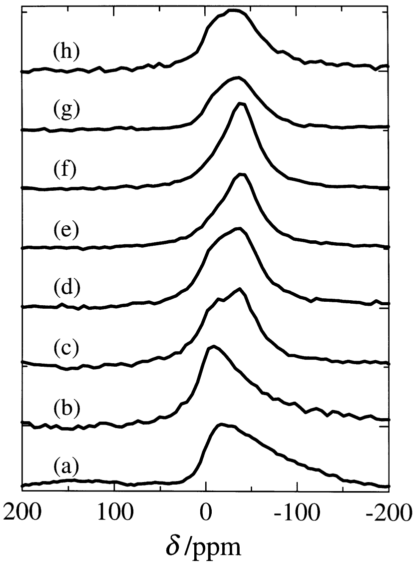

Fig. 2. ^{23}Na MAS NMR spectra of Na_2O-$3SiO_2$ glasses. (a) anhydrous sample. The glasses were hydrated at 80 °C for (b) 30 min, (c) 1 h, (d) 2 h, (e) 5 h, (f) 6 h, (g) 16.5, and (h) 24 h. The content of water in the glass is (b) 2.4 wt%, (c) 8.4 wt%, (d) 10 wt%, (e) 21 wt%, (f) 27 wt%, (g) 31 wt%, and (h) 39 wt%.

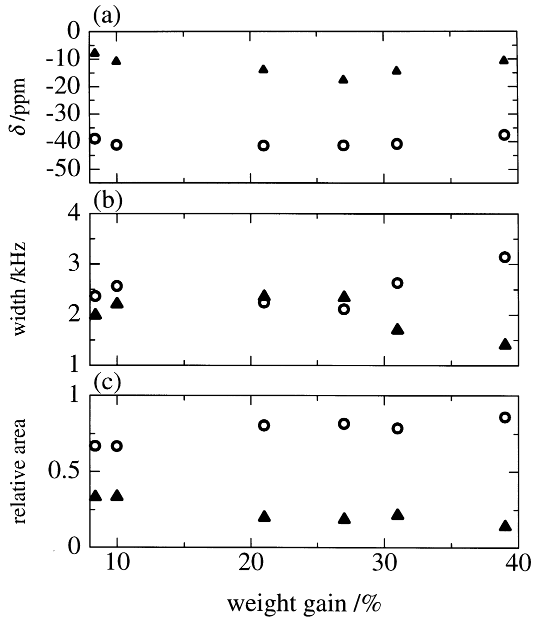

Fig. 3. The variation of the peak position, line width and relative area as a function of water content obtained, assuming two Gaussian peaks centered at –10 ppm (▲) and –40 ppm (○) (see the text).

observed in the spectra, indicating that the sodium environment does not change greatly. With further increase of water content (> 8.4 wt%, Fig. 2(c)), a new peak, centered at around –40 ppm appears. The intensity of this peak increases until the water content reaches 27wt% (Fig. 2(f)). The peak at around –10 ppm again appears above 30 wt% of water content (Fig 2(g) and (h)).

To estimate the fraction of the two sites observed in hydrated glasses, we attempted to fit the spectra in Figs. 2(c) - (h), assuming that these two sites are approximately represented by two Gaussian shapes centered at –10 ppm and –40 ppm. The position, width and proportion of the area obtained from the fittings are shown in Figure 3.

The temperature dependence of ^{23}Na MAS spectra for the sample (39%, Fig. 2(h)) is shown in Figure 4. As the temperature is lowered, the peak at around –40 ppm disappears, and finally a similar pattern as that of anhydrous glass is observed at –50 °C.

We carried out 2D ^{23}Na MQMAS NMR experiments to obtain more information on the environment of the two sites of Na observed in MAS spectra. In Fig. 5, 2D ^{23}Na MQMAS spectra of the anhydrous and the hydrous glass with high water content (39wt%, Figure 2(h)) are presented. The F_2 axis (horizontal) corresponds to the usual MAS dimension, and the F_1 axis (vertical) the isotropic one. All the spectra, both in F_1 and F_2 dimensions, are asymmetric [26]. One

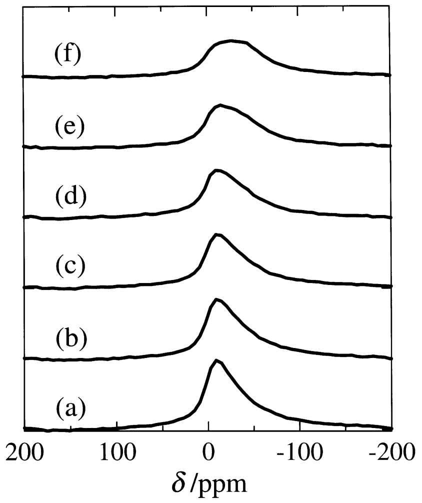

Fig. 4. Temperature dependence of ^{23}Na MAS NMR spectrum of hydrous glass (24 h, 39%; (h) in Figure 2). (a) –80 °C, (b) –50 °C, (c) –30 °C, (d) –10 °C, (e) 10 °C, and (f) 27 °C.

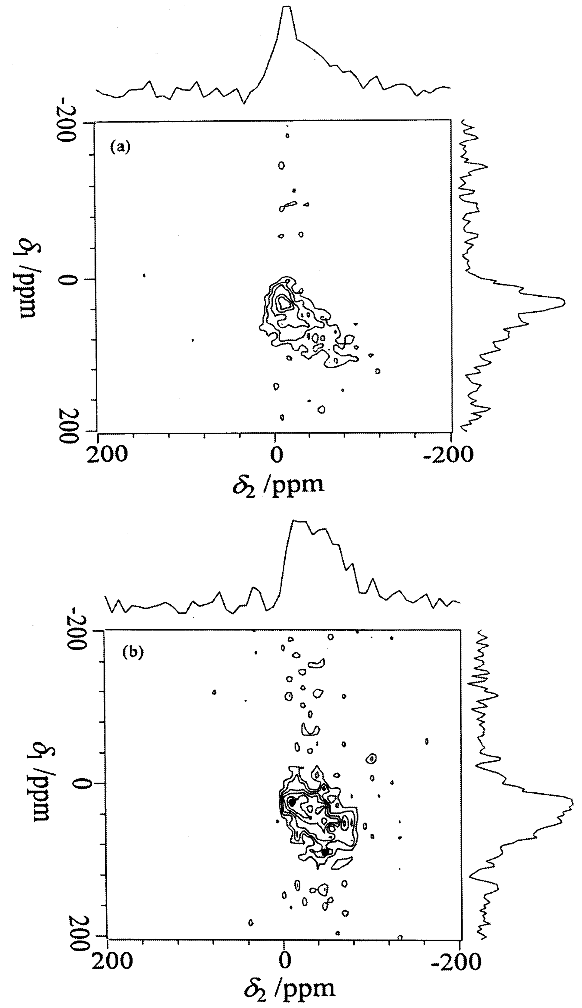

Fig. 5. ^{23}Na MQMAS spectra for (a) anhydrous glass and (b) hydrated glass (24 h, 39%). The lowest level of contour lines is 30% of the maximum point.

Table 1. The quadrupole coupling frequency (ν_Q) and the isotropic chemical shift (δ_{iso}) for ^{23}Na in the hydrous glass (39%) obtained from Figure 5(b).

	δ_1/ppm	δ_2/ppm	ν_Q/MHz	δ_{iso}/ppm
Na(1)	26.8	−10.2	0.6	4.2
Na(2)	91.6	−45.6	1.3	10.2

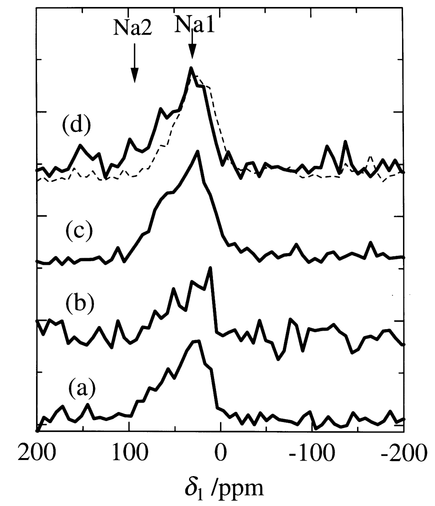

Fig. 6. F_1 projection of 2D MQMAS spectrum for (a) anhydrous glass and hydrous glass of with water concentration of (b) 2.4%, (c) 10%, and (d) 39%.

of the possible reasons for this asymmetry is that the efficiency of the triple quantum excitation depends strongly on the strength of the quadrupolar coupling constant, leading to the asymmetric spectra [12]. It is also possible that the distribution of δ_{iso} and ν_Q is asymmetric in the case of sodium in glasses [11, 12]. Figure 6 shows the variation of the F_1 projection with the water content in the sample. The intensity of the F_1 projection in 50 - 100 ppm seems to increase with the hydration time. In Fig. 5(b), the 2D signal, corresponding to this region, has a maximum at about −40 ppm in F_2 (see Fig. 5). With decrease in temperature, the intensity in the region between 50 ppm to 100 ppm in F_1 decreases, as shown by the dashed line. This corresponds to the fact that the signal of Na(2) in MAS spectra disappears at low temperature.

It was possible to find the point where the signals from Na(1) or Na(2) reach maxima both in the F_1 and F_2 dimension. These maxima are shown by closed circles in Fig. 5(b), and their chemical shifts are listed in Table 1. From these values we estimated the isotropic chemical shift (δ_{iso}), and the nuclear quadrupole coupling frequency (ν_Q) for Na(1) and Na(2), using the procedure [10] as follows.

For $I = 3/2$, the center of gravity of a signal in F_1 and F_2 dimension (δ_1, δ_2) is expressed as

$$\delta_1 = \frac{17}{8}\delta_{iso} + \frac{10^6}{8}\frac{\nu_Q^2}{\nu_0^2}, \tag{5}$$

$$\delta_2 = \delta_{iso} - \frac{10^6}{10}\frac{\nu_Q^2}{\nu_0^2}, \tag{6}$$

where ν_0 is the Larmor frequency. Hence, δ_{iso} and ν_Q for each site can be obtained from the experimental values of its δ_1 and δ_2 by solving (5) and (6). The parameters thus obtained are also listed in Table 1.

Discussion

In the present work, two sites were found in hydrated glasses (> 8.4wt%), and their isotropic chemical shifts and quadrupolar coupling frequency are determined from ^{23}Na 2D MQMAS NMR spectra. The values of δ_{iso} and ν_Q for ^{23}Na in sodium silicates and sodium hydrous silicates have already been determined by a few authors [27, 28]. Angeli *et al.* [12] investigated a series of sodium silicate, sodium alumino-silicate crystals and found a good relationship between the bond distance Na-O ($d_{\text{Na}-\text{O}}$) and δ_{iso},

$$d_{\text{Na-O}}\ (\text{Å}) = -0.0119\delta_{\text{iso}} + 2.5912. \qquad (7)$$

Using (7), the Na-O distance for Na(1) and Na(2) is estimated to be 2.54 Å and 2.47 Å, respectively. Angeli has shown that the average Na-O distance in sodium silicate glass is about 2.5 Å, so that the values obtained here are reasonable. Unfortunately, such a difference is not enough to specify the chemical states because various possible species of sodium-silicate or sodium-hydrosilicate have the Na-O distance between 2.4 Å to 2.6 Å. The difference of ν_Q for the two sites are not enough to distinguish the chemical states either, as ν_Q for many types of sodium silicate crystals and sodium hydroxide overlaps within this region of ν_Q. Although the chemical states were not well determined by the use of the 2D MQMAS spectra, the valuable information has been obtained that Na(2) has a shorter $d_{\text{Na-O}}$ and larger ν_Q than Na(1).

We further discuss the origin of the two sites of sodium, by considering again the variation of the ^{23}Na MAS spectra with water content (Fig. 2). Since the peak position of Na(1) is similar to that in anhydrous glass, Na(1) exists in similar environments in the anhydrous bulk glass, being attached to non-bridging oxygen, $\equiv$Si-O$^-$. On the other hand, Na(2) must be related to the site interacting with water incorporated in the glass because the signal for Na(2) becomes prominent only for the glasses containing a relatively high amount of water (> 8.3wt%).

Our previous results on infrared and ^{29}Si, ^{1}H NMR spectra [8] have shown that a structural change in the glass matrix occurs, depending on the water concentration incorporated in the glass: i) depolymerization of the -O-Si-O- network takes place above 3% water, ii) a mobile proton, originated from molecular H_2O, exists in glass with a higher water content (> 7 - 8wt%). The mobile proton may exist in the microphase of water in the micropores created by the decomposition of the glass network, iii) a significant recombination of $\equiv$Si-OH occurs above 20% of water, which is the reason for the gelation. Considering such structural changes, we tentatively assign Na(2) to Na$^+$ existing in a water microphase having relatively high mobility. It may be reasonable that sodium ions have much shorter bond lengths with oxygen and higher nuclear quadrupole coupling frequencies because the polarizability of OH$^-$ should be much stronger than that of Si-O$^-$. This assignment for the site Na(2) is further supported by the fact that the signal from Na(2) disappears with decreasing temperature. It is very likely that water in a microphase freezes below 0 °C, and, as a result, sodium ions are segregated from the water phase. The segregated sodium should attach to a $\equiv$Si-O$^-$ unit by ion exchange with H existing as Si-OH.

The local structure of Na(2) in the hydrated glass is not well specified at present, but it may be similar to that in some hydrous sodium silicate crystals having layered structure, where sodium ions are coordinated by the water and exist between silicate layers (see e. g. [21]). In the case of hydrated glasses, sodium and water may exist in micropores, the sizes of which are larger than in the water layers of the crystals. The size of the micropores may be large enough to give rise to the mobility of sodium and water observed in the experiments.

In the present study, two different species of sodium were found by using ^{23}Na MAS and MQMAS spectra. The isotropic chemical shift and the quadrupole coupling frequency of each site were successfully determined from MQMAS spectra. A still remaining question is how a Na$^+$ ion coordinates to a water molecule. $^{23}\text{Na}\leftarrow{}^1\text{H}$ CP MQMAS [29, 30] and MQMAS / HETCOR [31] experiments should be very helpful in answering the question, which is left for future study.

Conclusion

Hydration processes at low temperatures in Na_2O-$3SiO_2$ glasses were investigated by ^{23}Na NMR. ^{23}Na MAS spectra show that there exist two sodium sites in different chemical environment in a hydrated glass

(> 8.4wt%). The temperature dependences of ^{23}Na MAS spectra show that the second site disappears diminishes below 0 °C. From 2D MQMAS NMR spectra, it was possible to estimate the isotropic chemical shift and nuclear quadrupole coupling frequency for each site. From these results it is concluded that the second site in a hydrated glass (> 8.4wt%) is associated with sodium ions attached to water molecules.

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