Investigation of Al–O–Al sites in an Na-aluminosilicate glass

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Abstract. This paper reports the presence of Al–O–Al linkages in an aluminosilicate glass where Si/Al = 1 by using 2D ^{17}O triple quantum MAS NMR technique (3Q MASNMR). The experiments were performed at external magnetic fields of 8·4 and 14·4T. Despite ^{17}OMAS NMR spectra of the sample in both fields do not give much information about the different kinds of linkages in the sample, 3Q MAS NMR spectrum shows clear evidence that there are some amounts of Al–O–Al linkages in the sample giving two completely resolved peaks. These two peaks were attributed to the Si–O–Al and Al–O–Al linkages on the basis of their chemical shifts and, quadrupolar coupling constants which are quite sensitive to the local structure.

Keywords. ^{17}O MAS NMR; aluminosilicates; Al–O–Al; quadrupole coupling constant; asymmetry parameter.

1. Introduction

Aluminium containing glasses can be abundantly found in nature and they are also the most common man made glasses. Therefore, studies on the structure of these glasses are quite important for materials science and, earth science. It is generally accepted that the network of aluminosilicate glasses consists of SiO_4 tetrahedral and AlO_4 tetrahedral building blocks. In aluminosilicate glasses the distribution of aluminium–oxygen tetrahedra is such that the aluminium–oxygen tetrahedron tends to connect to four silicon–oxygen tetrahedra, i.e. aluminium–oxygen tetrahedra avoids direct links to other such tetrahedra. This arrangement is called aluminium avoidance or Lowenstein's (1954) rule. On the other hand in some aluminosilicates where Si/Al < 1, there is an on going discussion on the structure and role of excess aluminium since there will not be enough alkali or alkaline earth oxides for charge balancing to compensate the excess negative charge of aluminium oxide. Day and Rindone (1962) suggested that the excess aluminium occurs in octahedral coordination while Lacey (1963) suggested a tricluster model for such glasses where three coordinated oxygen connect three tetrahedra. Stebbins and Xu (1997) claimed that non-bridging oxygen can be found in such systems leading to Al–O–Al linkage and suggested the formation of tricluster configuration. However, in general, the formation of triclusters in aluminosilicates is found to be not very likely by many researchers on the basis of numerous quantum chemical studies which have found that the combination of an Al–O–Al corner sharing tetrahedral linkage and a Si–O–Si linkage to be higher in energy than two Si–O–Al

linkages (Hass *et al* 1981; Navrotsky 1985) which indicates the instability of Al–O–Al linkages (Riebling 1966). On the other hand, these computational results are not in good agreement with the observations, since many crystalline framework silicates show considerable Al, Si disorder at high temperatures and must contain appreciable numbers of Al–O–Al linkages (Tossel 1993).

As well as other experimental techniques (e.g. EXAFS, Raman spectroscopy, XRD...) aluminosilicates have also been investigated by means of mainly ^{29}Si and ^{27}Al MAS NMR (DeJong *et al* 1983; Murdock *et al* 1985; Kirkpatrick *et al* 1986; Lippmaa *et al* 1986) and these investigations revealed that the aluminium is tetrahedrally coordinated in compositions at around M/Al = 1, where M = Li, Na, K, Ca and therefore, Lowenstein's rule was obeyed.

Although oxygen is the most abundant element in the aluminosilicates, the NMR study of ^{17}O has not attracted much attention due to its low natural abundance and its spin quantum number, $I = 5/2$, which causes the line broadening quadrupolar interaction. It has been shown that ^{17}O NMR is a promising method for studying the structure and bonding in these materials (Schramm *et al* 1983; Turner *et al* 1985; Mueller *et al* 1992). Especially ^{17}O NMR studies show that bridging oxygen (which connect two tetrahedra e.g. Si–O–Al, Si–O–Si) and non-bridging oxygen have distinctly different chemical shifts and quadrupolar coupling constants (Timken *et al* 1986; Walter *et al* 1986). However, lack of resolution of ^{17}O MAS NMR spectra due to broadening caused by the quadrupolar interaction prevented observation and detection of different types of bridging oxygen, in detail, in such samples until recently. Although the magic angle spinning (MAS) technique is a most frequently used technique in the solid state NMR to remove anisotropic line broadening interactions such as dipolar interaction, and chemical shift anisotropy, it is

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not efficient in removing the quadrupole interaction for the $I > 1/2$ nuclei. The development of multiple quantum magic angle spinning (MQMAS), double rotation (DOR) and dynamic angle spinning (DAS) techniques provided very detailed high resolution NMR spectra as demonstrated by recent work on zeolites and on glasses (Dirken *et al* 1997; Xu and Stebbins 1998). DOR (Samason *et al* 1988) involves the simultaneous spinning of the sample around two axis whereas DAS (Chmelka *et al* 1989; Chmelka and Zwanziger 1994) involves sequential spinning of the sample about two axis giving a 2D NMR spectrum. Although these two techniques have been successfully used to study nuclides such as ^{17}O (Farnan *et al* 1992), ^{23}Na, ^{27}Al (Samason *et al* 1988), they have some technical and practical problems. Frydman and Harwood (1995) proposed an alternative technique called MQMAS which uses the multiple quantum coherence. It does not require very difficult simultaneous sample spinning as in DOR or sequential spinning as in DAS. MQMAS enhances the resolution of the spectra for a quadrupolar nuclei based on the correlation of $< m, - m >$ multiple quantum transition to the central transition $< 1/2, - 1/2 >$. In an NMR experiment for a quadrupolar nucleus, the evolution for a $m \leftrightarrow - m$ spin coherence after excitation can be described by a multi-rank expansion of its phase, Φ (Medek 1995)

$$\Phi(m, \boldsymbol{b}, t) = 2mtv^{CS} + v_0^Q C_0^I(m) +$$
$$v_2^Q(\boldsymbol{q}, \boldsymbol{j}) C_2^I(m) P_2(\cos \boldsymbol{b}) t +$$
$$v_4^Q(\boldsymbol{q}, \boldsymbol{j}) C_4^I(m) P_4(\cos \boldsymbol{b}) t,$$

where

$$C_0^I(m) = 2m[I(I+1) - 3m^2],$$
$$C_2^I(m) = 2m[8I(I+1) - 12m^2 - 3],$$
$$C_4^I(m) = 2m[18I(I+1) - 34m^2 - 5],$$

are zero, second and fourth rank coefficients depending on the spin number and order of transition.

$$P_2(\cos \boldsymbol{b}) = \frac{(3\cos^2 \boldsymbol{b} - 1)}{2},$$
$$P_4(\cos \boldsymbol{b}) = \frac{(35\cos^4 \boldsymbol{b} - 30\cos^2 \boldsymbol{b} + 3)}{8},$$

are second and fourth order Legendre polynomials and

$$v_0^Q = [(e^2 qQ/h)^2(3 + \boldsymbol{h}^2)]/[10v_L[2I(2I-1)]^2],$$

is the isotropic or zero rank quadrupole shift. $v_2^Q(\boldsymbol{q}, \boldsymbol{j})$ and $v_4^Q(\boldsymbol{q}, \boldsymbol{j})$ are second and fourth rank angular dependent frequencies responsible for the observed line broadening (Medek *et al* 1995). In order to refocus anisotropic interaction and obtain high resolution spectra, second and fourth order Legendre polynomials should be removed. In an MQMAS experiment, MAS removes the second rank qua-

drupolar shift as well as dipolar interaction and chemical shift anisotropy. The remaining fourth rank quadrupolar shift is cancelled by choosing two different coherence orders $(m_i \leftrightarrow - m_i)_{l=1,2}$ and spins are allowed to evolve under the effects of these two transitions. However, it is still difficult to observe minor amounts of Al–O–Al linkages and lack of data on this kind of site in crystalline model compounds causes great difficulty for the characterization of these sites.

2. Experimental

Initial mixture of the sample was prepared by mixing appropriate amounts of $Si^{17}O_2$, $Na_2C^{17}O_3$, and $Al_2^{17}O_3$ which were already isotopically enriched in the range of 20–25% ^{17}O and grinding in a mortar. Then the mixture was placed into a platinum tube, which was then sealed at both ends by torch or arc welding, to prevent the oxygen exchange. The sealed platinum tube was placed in the high temperature-melting furnace and was heated up to 1610–1650°C which was sufficient to melt the mixture. In order to obtain homogeneous melts the platinum tube was left at that temperature for 3 h. Then the tube was taken out from the furnace and immediately placed in water to obtain fast cooling. The nominal composition of the glass was found to be $Na_2O–Al_2O_3–1 \cdot 4SiO_2$ with Si/Al = 0·7 from its ^{29}Si MAS NMR which was in good agreement with the result found in literature for these compositions (Lee and Stebbins 1999). Single pulse MAS experiments were performed at two fields, 8·45 T (48·8 MHz) and 14·4 T (81·3 MHz), spinning at about 10 kHz and 20 kHz, respectively. 1 μs pulse length and 1–2 μs pulse delay were used. The two-dimensional 3Q MAS NMR experiments were performed at 14·4 T by using the split $t1$ pulse program which provides the shearing free processing of the spectrum (Brown and Wimperis 1997). The pulse lengths used in this experiment are as follows: excitation pulse: 2·5 μs, echo pulse: 0·6 μs and detection pulse: 0·7 μs. The delay times between these pulses were taken as 0·77 μs, 1·23 μs and 999 μs for the delay between excitation and echo pulse, between echo and the detection pulse, and formation of echo, respectively. Spinning speed of 20 kHz was used. As an external reference tap water (for ^{17}O) was used in both experiments.

3. Results and discussion

Figures 1 and 2 show MAS NMR spectra of the sample for fields, 8·4 T and 14 T, respectively. Although the spectrum shown in figure 1 shows a shoulder on the right side, both spectra are broad and asymmetric because of the second order quadrupole line broadening so they do not give detailed information about the sample. The spectrum shown in figure 2 is much narrower than the first spectrum mainly as a result of the high magnetic field and high

spinning speed. According to these two spectra there are only Si–O–Al linkages in the sample and aluminium avoidance rule was obeyed. On the other hand triple quantum MAS NMR spectra, shown in figure 3, presents two well resolved peaks centred at about 20 ppm and 30 ppm in the MAS dimension. The main peak and the small peak can be attributed to Si–O–Al site and Al–O–Al site, respectively on the basis of their quadrupole coupling constants (Tossel 1993) and their chemical shifts (Dirken *et al* 1997; Stebbins 1999). The main peak has a typical quadrupolar lineshape and quite wide. The shape of the small peak (Al–O–Al site) is a narrow ridge aligned along the slope of about 1, and this indicates a range of distribution in isotropic chemical shift values. There is no evidence of the presence of Si–O–Si site in the sample, otherwise a third peak at lower position in the isotropic dimension would be observed. In order to find out the distribution of qua-

drupolar coupling constants for both sites, few slices were taken along the MAS dimension and lineshape simulations were performed on them. The simulations were performed by using Qmas ½ model of the Win-Fit module included in the Bruker Win-NMR program for the PC (Bruker 1997) and they are repeated many times to find the best fit. The lineshape simulation of a slice from the Si–O–Al site along the MAS direction and results of all simulations are given in figure 4 and table 1, respectively. The changes in the quadrupolar coupling constant of the Si–O–Al site is very small since it decreases from 3·16 MHz to 3·02 MHz which indicates a small distribution of Si–O–Al bond angles in the sample. These quadrupolar coupling constant values are in good agreement with the values calculated by Tossel (1993) for the Si–O–Al, Al–O–Al species. Although the MQ MAS NMR is not quantitative due to poor efficiency of zero to 3Q excitation and 3Q to single quantum conversion (Dirken *et al* 1997), the ratio of total Al–O–Al species to the Si–O–Al species is about 0·175/1 giving a rough estimate of the Al–O–Al linkages.

4. Conclusions

^{17}O MQ MAS NMR experiment provided valuable information on this material, since it proved the presence of Al–O–Al site in the sample in which according to the composition about 17% of the oxygen in the sample are expected to be in the Al–O–Al site. 3QMAS spectra are not quantitative, because the efficiency of the triple quantum excitation and that of conversion to the observed NMR signal depend on quadrupolar coupling constant. However, this result may lead us to consider the presence of OAl$_3$ or OAl$_2$Si triclusters in this kind of glasses with the
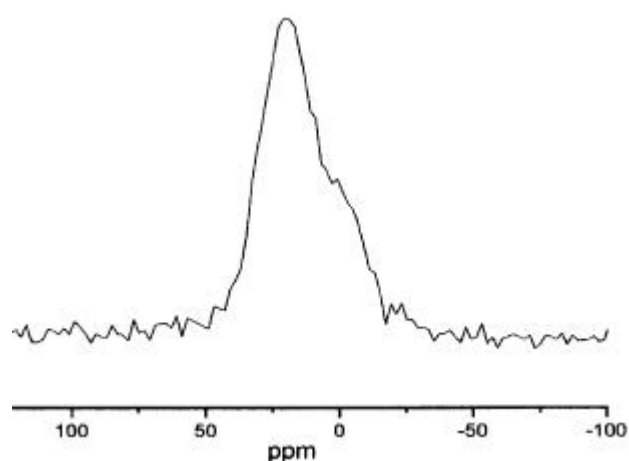

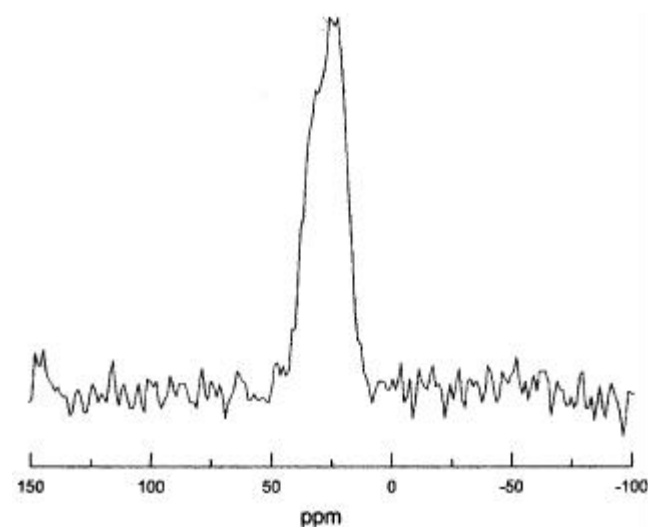**Figure 1.** O–17 MAS NMR spectrum of Na-aluminosilicate at 8·4 T.

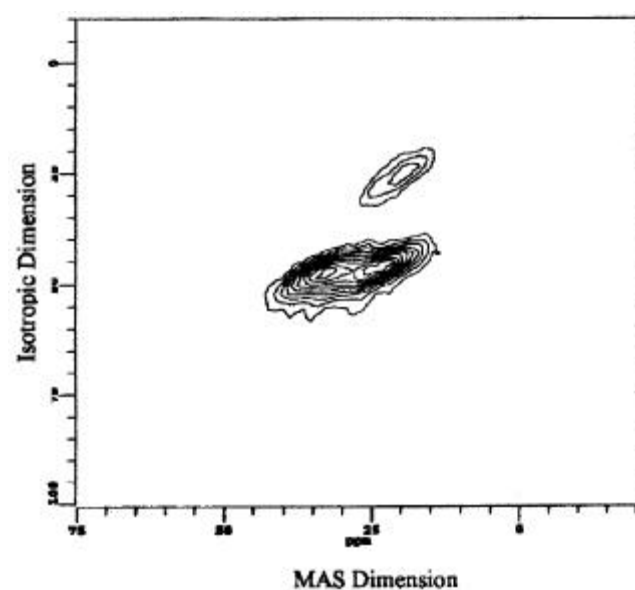**Figure 2.** O–17 MAS NMR of Na-aluminosilicate at 14·4 T.

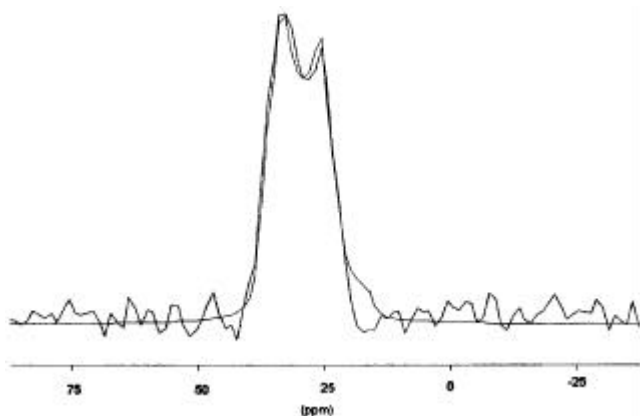**Figure 3.** O–17 3Q MQMAS NMR spectrum of Na-aluminosilicate glass at 14·4 T.

Figure 4. The simulation of a slice (slice 125) from Si–O–Al site along the MAS dimension.

Table 1. ^{17}O quadrupolar parameters of two sites in Na-alu-minosilicate glass obtained from the 3Q MAS NMR experiment. The slices were taken along the MAS dimension.

Site	C_Q (± 0·3 MHz)	h (± 0·1)	d (± 3 ppm)
Si–O–Al slice123	3·16	0·39	42
Si–O–Al slice125	3·13	0·42	39
Si–O–Al slice128	3·02	0·46	31
Al–O–Al	2·45	0·55	26

Si/Al ratio smaller than unity. The range bond angle distribution of the sample is quite narrow for the Si–O–Al site and it is difficult to obtain whether it follows the above equations or not.

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