The Structure of Glasses Studied by MAS-NMR Spectroscopy of Quadrupolar Nuclei *

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High-resolution solid state NMR spectroscopy of quadrupolar nuclei (preferentially ^{11}B and ^{27}Al) has been employed to study the microstructure of glasses. Importance has been attached to the extraction of the fundamental NMR parameters like chemical shift, quadrupole coupling constant etc., from the spectra, first of all by applying satellite transition spectroscopy. Exemplary results are represented for ternary oxide glass systems such as $K_2O–Al_2O_3–SiO_2$, $B_2O_3–Al_2O_3–P_2O_5$, $Na_2O–B_2O_3–SiO_2$ and $Na_2O–B_2O_3–Al_2O_3$.

Key words: MAS-NMR Spectroscopy, Quadrupole Satellite Transitions, ^{27}Al NMR, ^{11}B NMR, Glasses (Microstructure).

1. Introduction

Application of modern high-resolution solid state nuclear magnetic resonance (NMR) techniques in combination with increased magnetic fields and advanced data-processing led to a dramatic growth in structural investigations of glasses during the past 15 years [1]. Magic angle spinning (MAS) methods have been most successful for spin – ½ nuclei, but quadrupole nuclei like ^{11}B, ^{23}Na, and ^{27}Al, important in glasses, were often thought to have less significance, in particular since the fundamental NMR parameters may not be accessible. The spectra of quadrupolar nuclei suffer from the residual broadenings of second-order quadrupole effects and distributions of both chemical shift and quadrupole coupling parameters.

It is the purpose of this paper to show for a number of special ternary oxide glasses that many problems opposing an extensive employment of high-resolution spectroscopy to disordered materials can be overcome. ^{11}B and ^{27}Al MAS-NMR will especially be considered, and most studies have been carried out using satellite transition spectroscopy (SATRAS) [2]. This method is simpler and less expensive than the more sophisticated double rotation (DOR [3]) and dynamic angle spinning (DAS [4]) techniques. It is particularly well-suited for applications of the ^{27}Al resonance [5], but in addition to suitable computer programs it has also been shown to deliver reliable parameters for ^{11}B [6]. Here rather few ^{11}B MAS-NMR studies exist so far, although between 1958 and 1982, in the age of wideline cw techniques, ^{11}B NMR was the most important NMR probe for glasses, especially employed by Bray et al. in a large number of rather detailed studies [7]. More recently, DAS has been applied quite successfully to boron in borate glasses by Zwanziger et al. [8].

In the present paper the MAS-NMR of quadrupolar satellite transitions is exemplified by crystalline and glassy samples, and the procedure of data evaluation will be briefly explained. Results will be presented for both molten and sol-gel prepared glasses. ^{27}Al MAS-NMR spectroscopy was applied to measure chemical shifts, quadrupole couplings and aluminium coordination in $K_2O–Al_2O_3–SiO_2$ glasses [9] to elucidate some early c.w. data in molten glasses [10]. Both ^{27}Al and ^{11}B MAS-NMR was employed to examine chemical shifts and concentrations of four-, five- and six-coordinated aluminium and the environment of boron in $Al_2O_3–B_2O_3–P_2O_5$ glasses [9]. ^{11}B (in addition to ^{29}Si) MAS-NMR spectroscopy was used to characterize structural developments of gel-derived $Na_2O–B_2O_3–SiO_2$ systems [11] and to compare the data and structural models with molten borosilicate glasses [12, 13]. In $Na_2O–B_2O_3–Al_2O_3$ glasses CP-MAS and REDOR in addition to SATRAS provide details of connectivities between various structural units [14].

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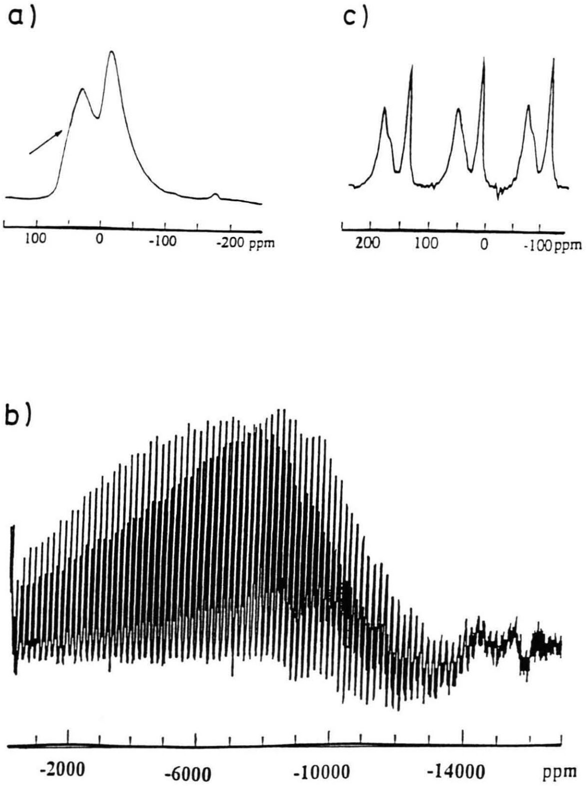

Fig. 1. ^{27}Al MAS-NMR spectrum of a 20 Al_2O_3–80 SiO_2 glass: a) central transition, b) right hand part of the interior satellite transition rotational sideband pattern, c) series of three selected rotational sidebands in an expanded scale. The following parameters were extracted using Eqs. (1) and (2): $\delta_{iso}(AlO_4) = 71$ ppm and 50 ppm (double peak), $C'_Q(AlO_4) = 6.0$ MHz and $\delta_{iso}(AlO_6) = 7.0$ ppm.

2. MAS-NMR of Quadrupolar Satellite Transitions

^{27}Al MAS-NMR spectra were measured at 78.2 MHz, ^{11}B MAS-NMR spectra at 96.3 MHz with a Bruker CXP FT spectrometer operating at 7 T. Extremely short pulses of 0.6 μs were used in order to excite a large spectral range of about 300 to 1600 kHz. For some samples with extremely large quadrupole couplings the radio-frequency irradiation was set about 500 kHz off-resonance to excite one half of the sideband spectrum completely. Rapid rotation at rates as high as 15 kHz was achieved with a high-speed MAS probehead. Figure 1 shows as an example some ^{27}Al MAS-NMR spectra of an aluminosilicate glass with different aluminium environments distinguished by strong quadrupole interactions. The central transition CT usually measured (a) reveals poor resolution. The interior satellite transition ST is represented by the sideband pattern (b) indicating slightly different quadrupole widths of the two signal components. The three selected sidebands shown in an expanded scale (c) have much better resolution than the CT.

Our second example (Fig. 2) refers to the ^{11}B MAS-NMR in a borosilicate glass, where two boron environments exist which cannot be separated in the CT. Four-coordinated boron is distinguished by first-order quadrupole interactions: both the CT and the ST (O. order sideband) appear at the same positions (chemical shift δ_{iso}). But for three-coordinated boron the centres of gravity $\delta_{CG}(m)$ of both transitions is

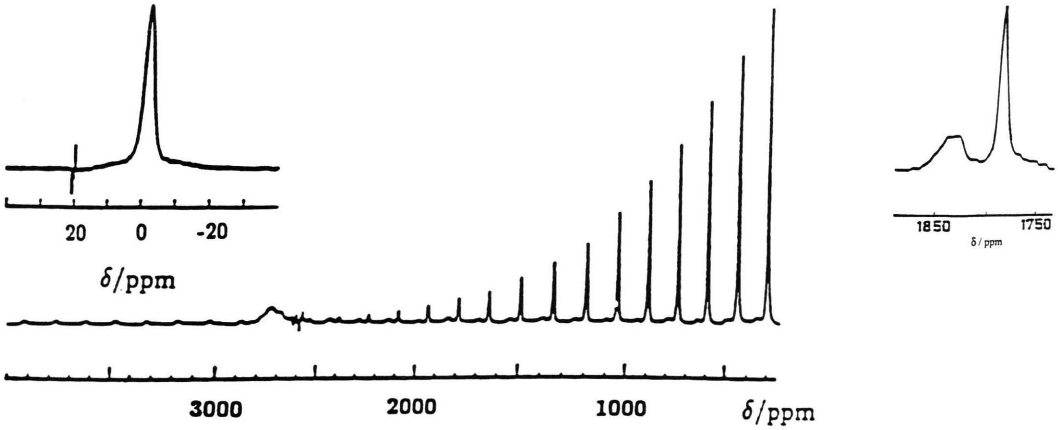

Fig. 2. ^{11}B MAS-NMR spectrum of a 12 Na_2O-13 B_2O_3-75 SiO_2 glass: the central transition (*left*), the satellite transition sideband pattern and one sideband (*right*) are shown. The following parameters were extracted: $\delta(BO_3) = 15.2$ ppm, $C'_Q(BO_3) = 2.7$ MHz, $\delta(BO_4) = -1.8$ ppm, $C'_Q(BO_4) = 0.52$ MHz, fraction of four-coordinated boron $N_4 = 0.76$.

shifted as a consequence of second-order quadrupole coupling.

Second-order quadrupole effects broaden the MAS spectra as shown in Figs. 1 and 2 and shift the position of both the CT and the STs away from δ_{iso} towards their respective centres of gravity.

$$\delta_{\mathrm{CG}}(m) = \delta_{\mathrm{iso}} + \delta_{\mathrm{QS}}(m)\,. \tag{1}$$

The CT belongs to $m = 1/2$, the interior STs belong to $m = 3/2$ or $m = -1/2$. The quadrupole shift was already calculated by Samoson in 1985 [15]

$$\delta_{\mathrm{QS}}(m) = -\frac{3}{40}\frac{C_{\mathrm{Q}}'^{2}}{\nu_0^2}\frac{I(I+1) - 9\,m(m-1) - 3}{I^2(2I-1)^2}\,, \tag{2}$$

as well as the relative width of the lines due to second-order quadrupole interaction

$$\Delta(m) = \frac{3}{128}\frac{C_{\mathrm{Q}}^{2}}{\nu_0^2}\frac{6I(I+1) - 34\,m(m-1) - 13}{I^2(2I-1)^2}\,. \tag{3}$$

C_{Q}' contains an influence of the asymmetry parameter η and may become up to 15% larger than the quadrupole coupling constant $C_{\mathrm{Q}} = e^2 qQ/h$ if η varies from 0 to 1

$$C_{\mathrm{Q}}' = C_{\mathrm{Q}}\sqrt{1 + \frac{1}{3}\eta^2} \tag{4}$$

ν_0 is the NMR frequency.

For ^{27}Al with $I = 5/2$, Eq.(3) predicts for the interior ST a gain in resolution of about 3 which can be realized by a comparison of the CT and ST signals of Figure 1. For ^{11}B with $I = 3/2$ there is no essential gain in resolution, but the overlapping signals of the CT due to three- and four-coordinated boron become separated (cf. Figure 2). Using (1) and (2) the relevant NMR parameters can be extracted from the spectra:

$$\left.\begin{aligned}\delta_{\mathrm{iso}} &= \frac{8}{9}\delta_{\mathrm{CG}}\left(\frac{3}{2}\right) + \frac{1}{9}\delta_{\mathrm{CG}}\left(\frac{1}{2}\right)\\ C_{\mathrm{Q}}' &= 12.17\,\nu_0\sqrt{\delta_{\mathrm{CG}}\left(\frac{3}{2}\right) - \delta_{\mathrm{CG}}\left(\frac{1}{2}\right)}\end{aligned}\right\}\ {}^{27}\mathrm{Al}\,(I = 5/2)$$

$$\left.\begin{aligned}\delta_{\mathrm{iso}} &= \frac{1}{3}\delta_{\mathrm{CG}}\left(\frac{3}{2}\right) + \frac{2}{3}\delta_{\mathrm{CG}}\left(\frac{1}{2}\right)\\ C_{\mathrm{Q}}' &= 3.65\,\nu_0\sqrt{\delta_{\mathrm{CG}}\left(\frac{3}{2}\right) - \delta_{\mathrm{CG}}\left(\frac{1}{2}\right)}\end{aligned}\right\}\ {}^{11}\mathrm{B}\,(I = 3/2)$$

The chemical shifts are referenced to $AlCl_3$ and $BF_3 \cdot Et_2O$, respectively.

Further examples elucidating the procedure were already given elsewhere [6, 11, 16]. In crystals with small quadrupole couplings (example: ^{27}Al MAS-NMR in $Al(PO_3)_3$ with $C_{\mathrm{Q}}' = 0.30$ MHz) the difference between $\delta_{\mathrm{CG}}(3/2)$ and $\delta_{\mathrm{CG}}(1/2)$ is insignificant and information on the quadrupole parameters can also be extracted from the envelope of the whole sideband pattern. For the modifications andalusite and sillimanite of Al_2SiO_5 with strong quadrupole interactions, however, the relevant parameters can neither be obtained from the CT nor from the pattern, but only from the ST spectra. As far as the ^{11}B MAS-NMR of glasses is concerned, if there are large contributions of three-coordinated boron ($C_{\mathrm{Q}}' \approx 2.7$ MHz) in addition to four-coordinated boron ($C_{\mathrm{Q}}' \approx 0.6$ MHz), analysis of the ST is helpful in addition to a computer simulation of the CT using (2). For small threefold contributions, only the separated components of the ST look promising.

3. ^{27}Al MAS-NMR Studies of K_2O–Al_2O_3–SiO_2- and Al_2O_3–B_2O_3–P_2O_5-Glasses

Alkali aluminosilicate glasses belong to the first glassy systems that have been studied by means of broadline NMR [10]. Dramatic asymmetric line broadenings were observed when the molar ratio K_2O/Al_2O_3 dropped below 1, but at that time it was not possible to distinguish between aluminium with different coordinations and between the strength and the distribution of the nuclear quadrupole interaction. Quantitative analysis is now possible using the procedures outlined in the last Section. Figure 3 shows some selected spectra revealing that aluminium occurs only four-coordinated as long as the K/Al ratio does not become extremely small. Only the sample shown at the bottom contains more than 30% AlO_6 units. $\delta_{\mathrm{iso}}(AlO_4)$ increases with the Al_2O_3 content from 57 ppm to 66 ppm, but more important is the behaviour of the quadrupole parameter C_{Q}' shown in Figure 4. The stepwise increase of the static linewidth described in the 1968 paper [10] looking very similar to the behaviour of C_{Q}' can indeed be attributed to the EFG and not to the different aluminium coordinations.

A detailed discussion of the structure of this glass system will be given elsewhere [16]. But here we may already state that at sufficiently high alkali concentrations ($x > 1.5$) the network consists of AlO_4 and SiO_4

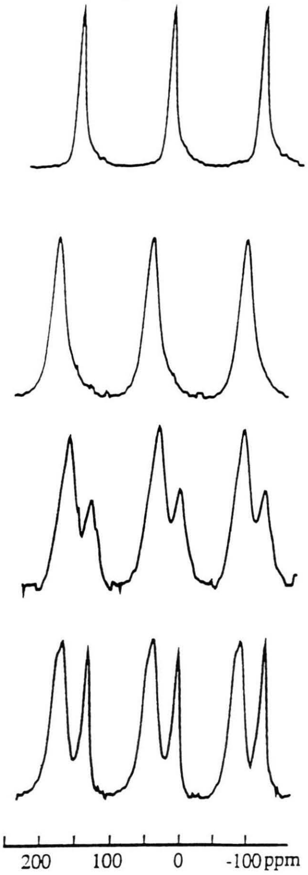

Fig. 3. ^{27}Al MAS-NMR ST spectra (three selected side-bands) of some K_2O–Al_2O_3–SiO_2 glasses containing 70 mol% silica. The composition in mol% is indicated.

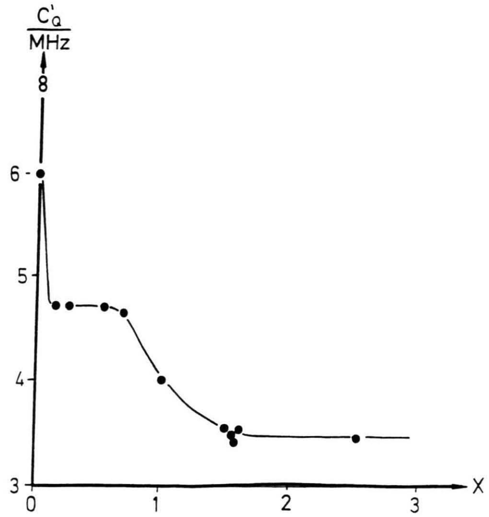

Fig. 4. Quadrupole coupling parameter C_Q' for K_2O–Al_2O_3–SiO_2 glasses plotted against x = mol% K_2O/mol% Al_2O_3.

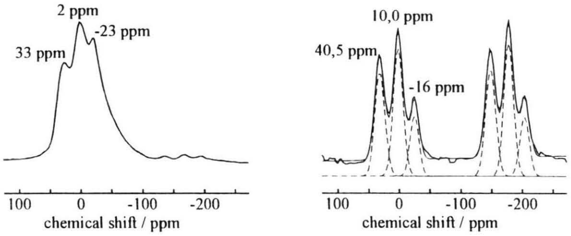

Fig. 5. ^{27} Al MAS-NMR CT (*left*) and ST spectra (*right*) of a 20 Al_2O_3-20 P_2O_3-60 P_2O_5 glass. The chemical shift values of the centres of gravity $\delta_{CG}(1/2)$ and $\delta_{CG}(3/2)$ are indicated. The fractions of the three signals appear to be 38:46:16 as extracted from the ST (cf. dotted lines) after correction (see text).

tetrahedra. For $x < 1.5$ the $Al(OSi)_4$ units become more and more distorted, possibly in a first step by the formation of "triclusters" to account for the charge balance constraints. Only for $x < 0.25$, in a second step interstitial Al^{3+} occurs and the AlO_4 tetrahedra are then charge-compensated by K^+, Al^{3+} and cluster formation.

Glasses in the system Al_2O_3–B_2O_3–P_2O_5 are of basic interest because all the constituents may act as glass formers. They exist in the phosphorus-rich region, approximately limited by the crystalline compounds $AlPO_4$, BPO_4 and $Al(PO_3)_3$. As revealed by the ST spectra (cf. example in Fig. 5) ^{27}Al MAS-NMR signals appear at 40 ppm, 9 ppm and −17 ppm assigned to four-, five- and six-coordinated aluminium with phosphorus in the second coordination sphere. Different from the aluminosilicate glasses, both chemical shift and quadrupole coupling data (all the C_Q's between 2.5 MHz and 2.7 MHz) do not change with composition. But in contrast, the concentrations of AlO_4, AlO_5 and AlO_6 units change greatly. They can be deduced from the spectra if certain corrections are applied (different quadrupole widths of the sideband pattern, bandwidth characteristics of the probe).

Additional information on these systems was obtained from the ^{11}B and ^{31}P MAS-NMR. Boron occurs only four-coordinated. The observed chemical shift of ^{31}P (referenced to H_3PO_4) varies between

−41 ppm and −29 ppm depending on the glass composition. AlO_4 and BO_4 units linked to PO_4 cause shifts in positive direction, AlO_6 those in negative direction. A model of randomly distributed and three-dimensionally connected PO_4, AlO_4, and BO_4 tetrahedra (formation of neutral BPO_7 and $AlPO_7$ units) may explain the structure, where the excess oxygen is charge-compensated by $(AlOP^4)_5$ and $(AlOP^4)_6$ coordinations.

4. ^{11}B MAS-NMR Studies of Alkali Borosilicate Glasses

Using the potential of ^{11}B MAS-NMR spectroscopy in addition to ^{29}Si MAS-NMR and ^{23}Na MAS-NMR, re-investigation of alkali borosilicate glasses [13] led to new conclusions. Structural developments of gel-derived glasses were studied [11] and the products were compared with conventional molten glasses [12, 13]. Figure 2 of the second Section was an example of a ^{11}B spectrum in the presence of boron in both trigonal planar and tetrahedral coordination. The quadrupole parameters $C'_Q(BO_3) = 2.4 - 2.7$ MHz and $C'_Q(BO_4) = 0.4 - 0.8$ MHz are characteristic of three- and four-coordinated boron, but they are not useful to distinguish between different structural units of the same coordination at various compositions. Detailed information was rather obtained from the exact determination of chemical shifts $\delta_{iso}(BO_3)$ and $\delta_{iso}(BO_4)$.

For the sol-gel prepared glasses it was thus possible to observe the condensation, copolymerization and removal of hydrogen-containing groups by NMR studies at various intermediary steps of the heat treatment [11]. The final glass turns out to be rather similar to the molten product, but it is more homogeneous and there are a few more characteristic differences detectable by NMR. The whole set of data could be modeled by a uniform distribution of copolymerized SiO_4, BO_4, and BO_3 polyhedra.

Molten glasses were thought to be characterized by a certain intermediate range order and the random network hypothesis may not be valid. The model of Dell et al. [12] which assumes the existence of larger structural units depending on the composition in detail was entirely based on ^{11}B NMR measurements of N_4, the relative fraction of four-coordinated boron. Evaluation of the whole set of data ($\delta(BO_3)$, $\delta(BO_4)$, $\delta(SiO_4)$, $\delta(^{23}Na)$, N_4) led to a description of these glasses which emphasizes much more the random network character [13]. Such a conclusion can be drawn, e.g. from Figure 6. The chemical shift $\delta(BO_4)$ measured for a large number of glasses with different compositions can be described by a linear relationship with the silica and soda mole fractions. Addition of SiO_2 reduces the limiting shift of −0.62 ppm, that of Na_2O increases the shift of four-coordinated boron. Independent of the composition all the glasses follow this relation, except those which display phase separation (not shown). In contrast to sol-gel prepared alkali borosilicate glasses the NMR parameters depend directly on the sodium amount. In gel glasses there is a different influence of sodium on the microstructure.

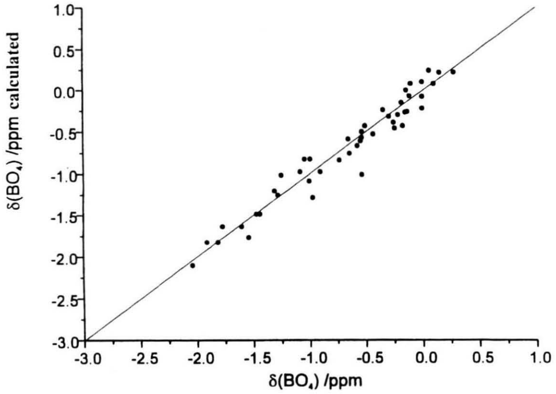

Fig. 6. Chemical shift of four-coordinated boron calculated by the equation $\delta(BO_4) = -3.4\, x_{SiO_2} + 2.8\, x_{Na_2O} - 0.62$ from the composition (not indicated in detail) of various molten $Na_2O-B_2O_3-SiO_2$ glasses in the whole glass-forming region plotted against the measured shift data. x_{SiO_2} and x_{Na_2O} are the corresponding mole fractions.

5. Aluminium-Boron Connectivities in $Na_2O-B_2O_3-Al_2O_3$ Glasses

A further promising step for studying the microstructure of ternary glass systems like those described above is the application of double resonance techniques to quadrupolar nuclei. CP-MAS and Rotational Echo Double Resonance [REDOR, 17] experiments involving both nuclei ^{11}B and ^{27}Al were carried out on "NABAL" glasses ($Na_2O-B_2O_3-Al_2O_3$) [14, 18]. These systems contain three- and four-coordinated boron and four-coordinated aluminium. The goal was to examine in addition to experiments like those described above the connectivities between AlO_4 tetrahedra on one hand and BO_3 trigonal planar and BO_4 tetrahedral units on the other hand by considering the heteronuclear dipolar coupling between both quadrupolar nuclei. In such an experiment the dipolar coupling, normally eliminated by MAS is re-introduced by suitable pulses. Those spins which experience this coupling do not contribute to the REDOR signal and they are detected by the difference signal. As a first result, it seems that aluminium tetrahedra are preferentially connected to trigonal boron units.

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