Probing the Structure and Crystallinity of a Lithium Silicate Glass by ^{29}Si Magic-Angle-Spinning NMR Spectroscopy

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It is now well established that high-resolution magic-angle-spinning NMR spectroscopy (MASNMR) can monitor the nature of short-range order in both non-crystalline and crystalline solids[1,2]. ^{29}Si-MASNMR studies of silicates have shown that the ^{29}Si chemical shift is related to the Si–O–Si angles and to interatomic distances[3]. In glasses, where a wide range of such structural parameters are simultaneously present, lineshapes provide information about the nature of the distribution functions[4]. We have found that useful information on the distribution of Si–O–Si angles may be obtained from ^{29}Si-MASNMR spectra of glasses in which the crystallinity varies from zero to 100%, as gauged by electron microscopy.

We have chosen lithium disilicate glass, thermally treated to yield a range of materials extending between the two extremes of 100% crystallinity and 100% non-crystallinity. Lithium disilicate, $Li_2O \cdot 2SiO_2$, is a particularly suitable material for such a study since its crystal structure is known[5], and no change of composition is observed on devitrification. Crystalline lithium disilicate consists of a double-chain arrangement of apex-shared SiO_4^{4-} tetrahedra in such a way that each Si atom has three equivalent silicon neighbors. Partly crystalline $Li_2O \cdot 2SiO_2$ contains minute microcrystals immersed in an amorphous matrix, apparent even in scanning electron micrographs, and is readily detectable by electron diffraction.

In recording the ^{29}Si-NMR spectra, we noted that the spin-lattice relaxation times T_1 of the nucleus were very different in the microcrystalline and non-crystalline regions; in the former case this was of the order of seconds while in the latter of the order of hours. This large difference in relaxation times makes it possible to distinguish between the two regions and measure the relative amounts of material in each. Whereas the spectrum of the crystalline part of the mixture can be obtained relatively easily, a spectrum comprising signals of both the amorphous and crystalline regions can be measured only if short pulses and long pulse delays are used, and we used 30° pulses separated by 90 min delays.

Even those samples which, by microscopy, appeared largely (80%) non-crystalline, contained traces of microcrystallinity, and hence the resulting spectrum (Fig. 1a) contains the characteristic, though somewhat broader signal at $\delta = -92$ from tetramethylsilane (TMS) superimposed upon a much broader background resonance, the chemical shift of which ranges from $\delta = -70$ to -120 and which is attributable to non-crystalline regions of the sample.

The total range of ^{29}Si-NMR chemical shifts in silicates lies between $\delta = -60$ and -120. This is split up into five intervals[2] corresponding to Si atoms in monosilicates, i.e. to isolated SiO_4^{4-} groups (denoted by Q^0), disilicates and

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chain end groups (Q^1), middle groups in chains (Q^2), chain branching sites (Q^3), and fully crosslinked framework sites (Q^4). Within each structural category the ^{29}Si chemical shift is correlated with the Si–O–Si bond angles and the interatomic distances. We conclude that, in agreement with the established structure, the sharp resonance at $\delta = -92$ is attributable to Q^3 groupings (chain branching sites), and the chemical shift corresponds to an Si–O–Si angle of ca. 135°. The single sharp resonance at $\delta = -61$ (x) is due to Q^0 (monosilicate) present as binder in the ZrO_2 magic-angle spinner.

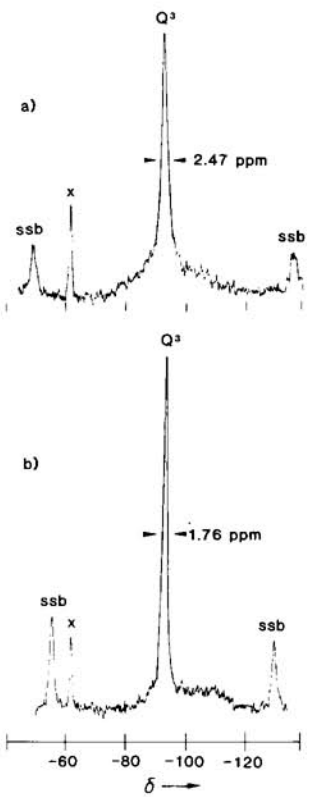

Fig. 1. ^{29}Si-MASNMR spectra (59.60 MHz, Bruker CXP-300). a) Partially crystallized lithium disilicate glass; b) almost completely crystalline $Li_2O \cdot 2SiO_2$. Samples spun at ca. 3.5 kHz in Andrew-Beams spinners made of Delrin. δ-values given in ppm relative to TMS branching sites.

There are also distinct spinning sidebands (ssb) equidistant from the main signal, which are due to chemical shift anisotropy. Their presence supports our assignment of the main signal as arising from Q^3 units; Q^4 (fully cross-linked framework sites) units resonate at a higher field and involve much smaller chemical shift anisotropy. Spinning sidebands from Q^4 sites in framework silicates are much less distinct than in the present Q^3 case. Finally, no Q^2 signals (corresponding to the termination of the double chain) are visible in the spectra, indicating that their concentration is low.

The range of resonances ($\delta = -70$ to -120) for the non-crystalline regions can be interpreted in several ways: 1) Q^1, Q^2 and Q^3 groups are present, 2) the Si–O–Si angles range from ca. 120 to 180° in the Q^3 groupings, and 3) the interatomic distances vary. Of these possibilities, a combination of 2) and 3) is the most likely explanation. The fact that the spectrum of the largely crystalline sample (electron diffraction studies) also contains a broad background resonance signifies the presence of some crystallographically disordered material. When the composition of a lithium silicate glass $Li_2O \cdot x\,SiO_2$ is varied by increasing x, a broad NMR signal is observed whose chemical shift approaches that of Q^4 units.

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