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Devitrification of sodium disilicate glass: a NMR study

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Several crystallographically non-equivalent structures of sodium disilicate are known to exist. Successive heat treatments of the sodium disilicate glasses show α-, β-, γ- and δ-$Na_2Si_2O_5$ as the devitrification products, depending upon the nature of heat treatment. At higher temperatures and for longer treatment times, only α-$Na_2Si_2O_5$ is observed but for intermediate temperature and time, α and β forms of the polymorphs are produced. For shorter times, all the polymorphs are formed. The results are verified using magic angle spinning nuclear magnetic resonance as well as X-ray diffraction. A way of estimating the unknown Si–O–Si mean bond angle of the polymorphs, with the help of the known values of the angles, is also presented. © *1998 Kluwer Academic Publishers*

1. Introduction

It is now well known that nuclear magnetic resonance (NMR) spectra of alkali silicate glasses provide useful information about the quantity and number of species of differing symmetry present in the glasses [1–5]. However, even in combination with magic angle spinning (MAS), NMR spectra of the species in glasses with very small structural differences (differences in bond angle, bond length) are indistinguishable, because the chemical shift difference is much less than the linewidth. For example, ^{29}Si spectra of $Na_2O \cdot 2SiO_2$ glasses [4] are difficult to interpret, particularly when the relative amount of one of the species is small. Moreover, the resolution of the ^{29}Si glass spectra is not sufficient to give information about the position and local order of its next nearest neighbour sodium ion. Thus the mechanism of the distribution of the Na^+ ion, apart from Si–ONa, is also impossible to interpret because of the range of sites of the species.

In an ordered material, such a subtle difference in structure cannot exist and it would be expected that MAS NMR spectra should provide well-resolved lines corresponding to different positions of the next nearest neighbour. According to an XRD study of sodium disilicate [6], there are six polymorphs, α_I, α_{II}, α_{III}, β, γ, δ-$Na_2Si_2O_5$, known to exist at 1.0 bar pressure but, so far, MAS NMR study of the crystalline system has found only one peak corresponding to α-$Na_2Si_2O_5$ [4, 7]. The purpose of this work was to study the various polymorphs of sodium disilicate, made by judicious choice of heat treatments, using MAS NMR. This technique is shown to be sensitive to the local environment of the ^{29}Si, particularly bond angle and bond length of the nearest and next nearest neighbours, in various polymorphs of $Na_2Si_2O_5$. The ^{29}Si chemical shifts of the polymorphs were also used to estimate the mean Si–O–Si bond angle.

2. Experimental procedure

Sodium disilicate glass was prepared as described by Dupree *et al.* [4] and the heat-treatment sequence under normal temperature and pressure used to produce glass ceramics from the base glass is shown in Fig. 1. The ^{29}Si broad line NMR and MAS NMR spectra were recorded on a Burker MSL 360 spectrometer. Samples for ^{29}Si nuclei were spun at 3–4 kHz and a π/6 pulse, followed by sufficient relaxation delay to unsaturate the signal, was employed to collect the spectra. Tetramethyl silane was used as a reference to set the chemical shift, $\sigma = 0$. An exponential line broadening of 5 Hz, i.e. effective increase in line width of about 0.02 p.p.m. was applied during the processing of the ^{29}Si MAS NMR spectra and that for static NMR spectra was 100 Hz, i.e. an increase in line width of about 0.45 p.p.m.

3. Results

The ^{29}Si MAS NMR spectra of the base and heat-treated sodium disilicate are shown in Fig. 1. Fig. 2 shows the static spectra of $Na_2O \cdot 2SiO_2$ base glass and that heat treated at 625 °C/12 h along with the MAS spectrum of the latter. The non-equivalent crystalline sites begin to appear for heat treatment 575 °C/6 h. The crystallization products in

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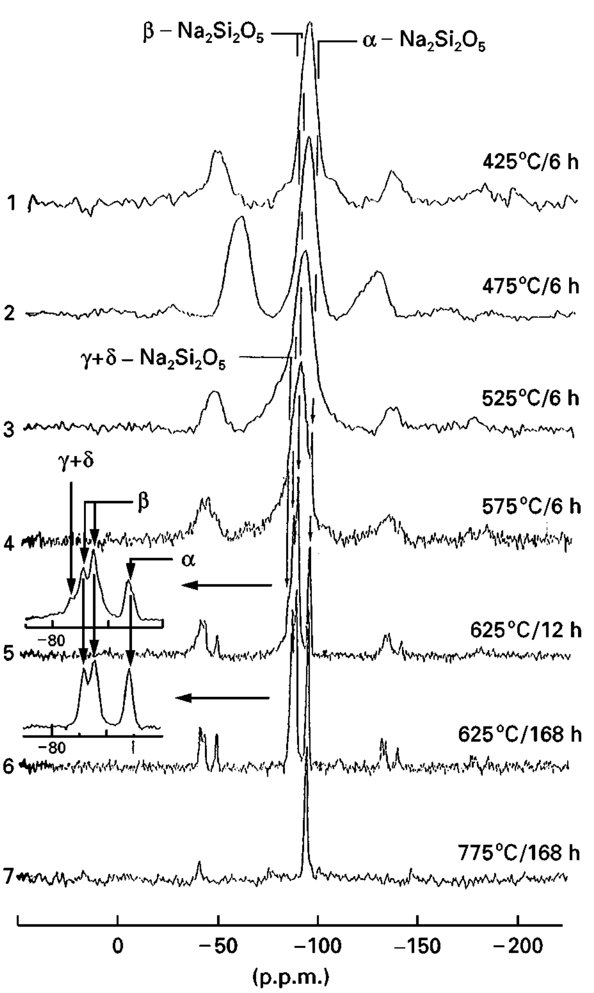

Figure 1 ^{29}Si spectra of heat-treated sodium disilicate glasses. The samples were taken from the same batch but heat treated separately at the indicated temperatures.

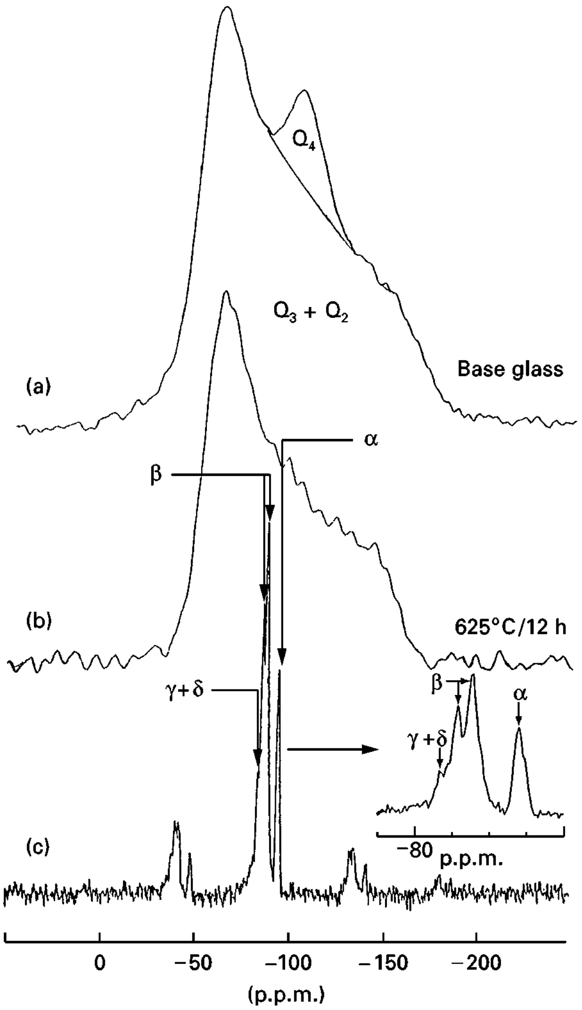

Figure 2 ^{29}Si static spectra of sodium disilicate: (a) base glass, (b) crystalline. (c) ^{29}Si MAS spectra of (b), and inset is an extended form of the centre band.

TABLE I Spectral parameters and Si–O–Si mean bond angle of $Na_2Si_2O_5$ polymorphs

Polymorph	Chemical shift $\pm$ 0.2 (p.p.m.)	FWHM $\pm$ 0.2 (p.p.m.)	Si–O–Si mean bond angle (deg)
α	− 93.6	1.4	149.5
β	− 87.4	1.8	136.8
	− 85.6	1.4	135.1
$\gamma + \delta$	− 83.8	[a]	132.7

[a] Not determined.

$Na_2O \cdot 2SiO_2$ heat treated at 625 °C/12 h are α_I, α_{II}, β and $\gamma + \delta$ phases. The NMR parameters and bond angles of the polymorphs are presented in Table I.

Fig. 3a shows the ^{29}Si chemical shift of various polymorphs as a function of mean sec(α'), where α' is the Si–O–Si bond angle. The bond angles for α- and β-$Na_2Si_2O_5$ are known and only with three points can a straight line be drawn with a degree of uncertainty. A correlation between them is found to be

$$\sigma = -132.5 - 33.3\sec(\alpha') \qquad (1)$$

where σ is the chemical shift. Fig. 3b shows the variation of chemical shift for a certain range of α'.

4. Discussion

The crystallization peaks due to different polymorphs started to appear for 575 °C/6 h heat treatment (Fig. 1). Among the six polymorphs of sodium disilicate, three of them belong to the α (α_I, α_{II}, α_{III}) group. The individual mean bond lengths and bond angle for the α-$Na_2Si_2O_5$ group are unknown and, from MAS NMR, only one peak at − 93.6 p.p.m. corresponding to this group is observed. It may be said that the local order of silicons in the α-group is essentially the same but in long-range order they are different. The effect of sodium site symmetry on silicons of the group is difficult to interpret from the ^{23}Na spectrum (not shown) because this material contains a variety of polymorphs in which the local order of sodium is almost impossible to distinguish. However, the small shoulders (Fig. 1c; enlarged scale of 625 °C/12 h) on the peak at − 93.5 p.p.m. may be due to the members of the α-$Na_2Si_2O_5$ family.

XRD data [8] show that β-$Na_2Si_2O_5$ does have two different silicon sites and this is confirmed by two well-resolved ^{29}Si resonances at − 87.5 and − 85.7 p.p.m. This resolution is also enhanced by the different coordinations of sodium, one is octahedral and the other one is trigonal biprism, as the next nearest neighbour of the two silicons. Thus the β form of

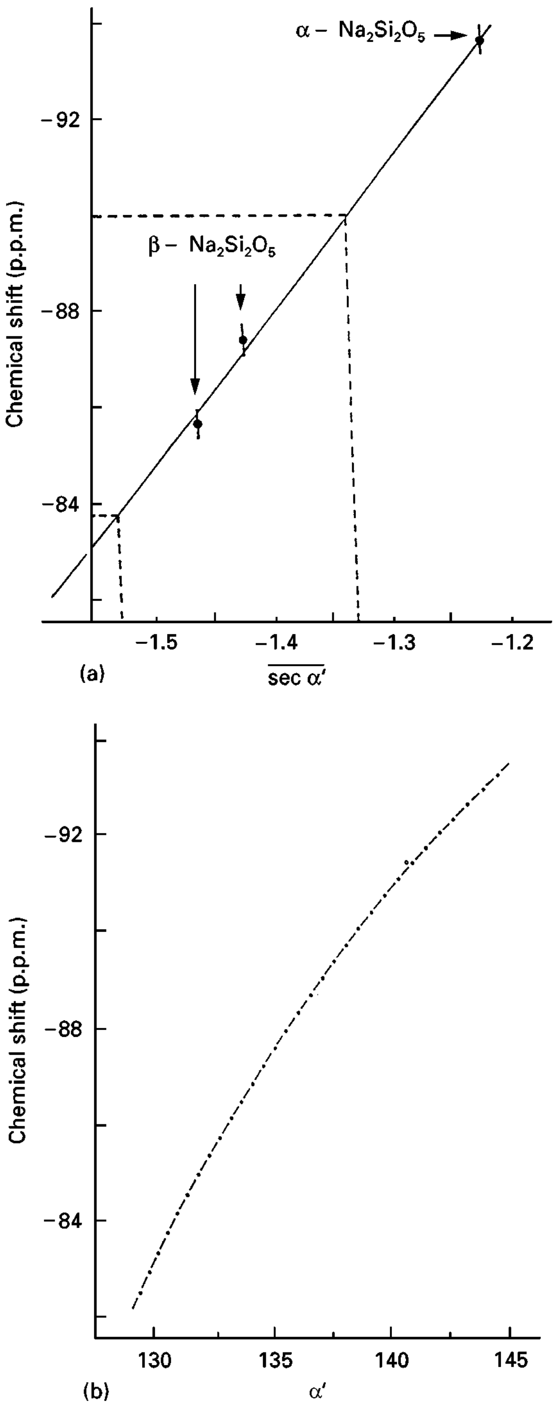

Figure 3 Variation of the ^{29}Si chemical shift with (a) mean sec(α′) and (b) α′, where α′ is the Si–O–Si bond angle.

sodium disilicate does exist and this is the first confirmation of the polymorph by using MAS NMR.

The $\gamma + \delta$ phase mixture is unstable [6, 9] and only α and β are observed for the heat treatment at 625 °C/168 h (Fig. 1f). All the $\gamma + \delta$ phase is converted to β phase, which is evident from the figure. The β-Na$_2$Si$_2$O$_5$ is also unstable [6, 9] and when the sample was heat treated at 775 °C/168 h, only α_1- and α_2-Na$_2$Si$_2$O$_5$ phases are observed. This is confirmed by XRD and the resonance position at − 93.6 p.p.m. which is close enough to the previously assigned peak (− 93.5 p.p.m.) for the α-family.

The mixture of γ and δ phases for the heat treament at 625 °C/12 h was noted by Williamson and Glasser [6]. According to their investigation, the subtraction of the δ-phase XRD pattern from the composite pattern of $\gamma + \delta$ phase yielded the XRD trace of the γ-phase. The XRD of the sample indicated the presence of these phases, and a relatively broader peak on the MAS NMR spectrum (Fig. 2) represented the gamma and delta phases. However, the reason for this poor resolution could be due to the small difference in the Si–O–Si and Si–O–Na bond lengths and bond angles in the phases.

The ^{29}Si static spectrum of base Na$_2$O · 2SiO$_2$ glass does show Q$_4$ resonance, but that of the crystalline one does not (Fig. 2) and is consistent with the result of Stebbins [3]. The Q$_4$ in the glassy state combines with Q$_2$ and forms Q$_3$ as $Q_4 + Q_2 = 2Q_3$ during devitrification. The static ^{29}Si spectrum of Na$_2$O · 2Si$_2$O$_2$ is a representation of an axially symmetric powder pattern from which it is not possible to infer the number of polymorphs formed during devitrification. However, in the case of MAS NMR spectra, the formation of α, β and a mixture of γ and δ phases are observed.

According to Smith and Baily [10] and Brown and Gibbs [11], the ⟨Si–O⟩ bond distance changes from 0.161 nm to 0.164 nm as the various Q_m ($0 \leqslant m \leqslant 4$) species grow in the glass system from Q$_4$ to Q$_0$ due to addition of metal oxide. The Chemical shift is a function of bond distance and bond angles [12, 13] and the former increases with the decrease of the latter [14]. These facts suggest the validity of Equation 1, and therefore the Si–O–Si mean bond angle for the species of unknown structure can be determined (Fig. 3). Using Equation 1, the mean bond angle for $\gamma + \delta$ is determined to be 132.7°. Thus NMR provides an estimate of the mean bond angle where the single-crystal study is not available.

5. Conclusion

The polymorphs of sodium disilicate are produced by judicious choice of heat treatments and they are confirmed by using MAS NMR and XRD. NMR results are in agreement with the previsouly presented XRD data. NMR chemical shifts of various polymorphs are sensitive to the Na$^+$ ion coordination, as well as bond angles and bond distances. Line widths are relatively narrower, i.e. better resolution is obtained for differently coordinated Na$^+$. Much further work is still possible on quadrupolar ^{23}Na, ^{17}O nuclei to obtain information about their local order, and work is in progress to present the results.

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Note: The authors regret the omission of reference to the paper by D. Heidemann, C. Hubert, W. Schwieger, P. Grabner, K-H. Bergk and P. Sarv, Z. Anorg. Allg. Chem 617 (1992) 169–177, which reports the Si-29 chemical shifts in crystalline alpha-sodium disilicate (− 94.3 ppm) and beta-sodium disilicate (− 88.6 ppm and − 86.7 ppm).

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