Nuclear Magnetic Resonance (NMR) Investigation of Glass Forming Reactions in the Binary Na_2O-SiO_2 system

A .R. Jones, R. Winter and G. N. Greaves
Department of Physics, University of Wales, Aberystwyth, Penglais, Aberystwyth, UK

I. H. Smith
Glass Melting Technology, Pilkington Technical Centre, Lathom, UK

The glass forming reactions of a model SiO_2-Na_2CO_3 raw glass batch has been studied by Magic Angle Spinning (MAS) NMR spectroscopy of ^{29}Si and ^{23}Na. The study is concerned with the mechanism of the reaction between quartz and sodium carbonate at 700°C to 1300°C. The batch reaction process observed comprises of three main stages. The initial stage involves a solid-state reaction between quartz and Na_2CO_3 grains that are in direct contact. Precipitation of an intermediate crystalline $Na_2O•SiO_2$ phase at the reaction interface is observed. The second stage commences with the melting of Na_2CO_3 and the wetting of the partially reacted quartz grains. The reaction continues until the quartz and Na_2CO_3 are fully reacted and only crystalline $Na_2O•SiO_2$ is present. The final stage is the melting of $Na_2O•SiO_2$ observed at 1090°C to produce a melt of the same nominal composition.

Introduction

MAS NMR spectroscopy has been used to follow the batch melting of a $1SiO_2$-$1Na_2CO_3$ molar ratio batch. MAS NMR has been extensively used to study both silicate glass and crystalline minerals[1,2,3,4,5]. The equal sensitivity to both glass and crystalline materials makes MAS NMR ideally suited to study partially melted glass batches[2]. ^{29}Si MAS NMR is sensitive to changes in the polymerisation of the material. The corner-sharing SiO_4 tetrahedra of quartz are designated Q^4, where Q^n refers to the SiO_4 tetrahedron with n bridging oxygens (BO). The reaction of alkali carbonates with quartz produces an interface where the SiO_4 network has been depolymerised, forming non-bridging oxygens (NBO) and therefore a range of Q^n species. Q^2 and Q^3 species would be equivalent to a glass (or crystal) of composition $Na_2O•SiO_2$ and $Na_2O•2SiO_2$ respectively.

Experimental

The model batch with 50mol% SiO_2 and 50mol% Na_2CO_3 was prepared from high purity quartz and 99% ^{13}C-enriched Na_2CO_3 (Euriso-Top, France), with 0.2wt% Fe_2O_3 added to enhance spin-lattice relaxation. Samples of 200mg of batch were heated in a Pt crucible at a rate of 10°C/min and air quenched from 700, 850, 950, 1090 and 1300°C. MAS NMR experiments were performed on the samples on a Bruker Avance DSX 400 spectrometer with a principal field strength of 9.4T. Spectra were acquired with a 4mm MAS probe spinning at 5kHz and 15kHz for ^{29}Si and ^{23}Na respectively. The chemical shifts are referenced to TMS for ^{29}Si and aqueous NaCl for ^{23}Na.

Results

Silicon-29

The ^{29}Si MAS NMR spectra for the series of partially melted samples heated to specified temperatures and quenched are show in Figure 1. The spectra clearly show that an increase in heat treatment promotes the formation of a second narrow peak at ~ -86ppm. This peak is due to crystalline Q^2 species ($Na_2O•SiO_2$). The spectrum of the 850°C sample with improved S/N of the intermediate phases (at the expense of the quartz peak) is shown in fig.2. The broad resonance peak centred at ~ -98ppm is attributable to glassy Q^3 ($Na_2O•2SiO_2$) phase. The formation of an increasing amount of glassy phase is observed as the sample is heated past the melting temperature of $Na_2O•SiO_2$. The sample heated to 1300°C illustrates the dramatic broadening of the resonance line due to the greater range of bond angles and bond lengths in the glassy $Na_2O•SiO_2$ structure compared to the crystalline equivalent. Some crystalline $Na_2O•SiO_2$ remains at 1300°C and is clearly seen as a narrow peak on top of the broad resonance peak.

Sodium-23

Some of the ^{23}Na MAS NMR spectra are shown in Fig. 3. The ^{23}Na spectrum of the raw glass batch i.e. Na_2CO_3 is characterised by two peaks in the range –23 to –60ppm. Increased heat treatment promotes the growth of a peak at ~30ppm due to $Na_2O•SiO_2$ and the demise of the Na_2CO_3 peaks. The spectra of the sample heated to 950°C is characterised by only one peak due to $Na_2O•SiO_2$. A broad peak reappears in the range –23 to –50ppm in the last spectra of the series. This broadness is due to the glassy phase that was evident in the ^{29}Si spectra. Such broadness is also seen in the spectra of the 850°C sample when the difference spectrum is obtained (not shown) by subtracting the ^{23}Na spectrum of the raw batch.

Disscussion

The first step of the reaction between quartz and Na_2CO_3 taking place at 700°C is the formation of crystalline $Na_2O•SiO_2$ by solid-state reaction. This is shown both in the ^{29}Si spectrum with the line appearing at ~-86ppm and by the ^{23}Na spectrum with the line appearing at ~30ppm. The formation of $Na_2O•SiO_2$ continues as a function of heating at the expense of the quartz and Na_2CO_3. The first occurrence of a glass phase is observed at 850°C, therefore indicating the formation of a silicate melt. This corresponds to the broad peak centred at ~ -98ppm and corresponds to the chemical composition of $Na_2O•2SiO_2$. The formation of this glass phase could either be due to the melting of an equivalent crystalline phase or by the further reaction of the $Na_2O•SiO_2$ with quartz. Crystalline $Na_2O•2SiO_2$ melts at ~874°C, therefore it is thermodynamically possible for this compound to precipitate following the reaction of quartz and Na_2CO_3 between 700°C and 850°C. This would then melt when approaching its actual melting point producing the glass phase observed after quenching. Alternatively a reaction at the interface of the $Na_2O•SiO_2$ and quartz could also lead to the formation of $Na_2O•2SiO_2$. Since no samples have yet been heated to temperatures in the region 700°C to 850°C it is not possible to confirm either mechanism. In-situ X-ray diffraction studies are presently being carried out which can confirm the reaction mechanism.

By 950°C both quartz and Na_2CO_3 have fully reacted since the signal at ~ -116ppm has disappeared from the ^{29}Si spectra and no Na_2CO_3 contribution is present in the ^{23}Na spectra.

The sample is composed only of crystalline $Na_2O•SiO_2$ at 950°C. The silicate melt ($Na_2O•2SiO_2$) observed at 850°C is no longer present. This indicates a reaction of $Na_2O•2SiO_2$ with Na_2CO_3 to form crystalline $Na_2O•SiO_2$, which would be the most thermodynamically stable product at this temperature.

A significant change in the ^{29}Si spectra appears above the melting point of $Na_2O•SiO_2$. Broad resonance peaks due to glass phases are observed corresponding to the melting of the crystalline $Na_2O•SiO_2$ structure. The broadness of the peak indicates the disordered environment of the Si atoms in the newly formed melt.

Conclusion

^{29}Si and ^{23}Na MAS NMR has been used to study the reactions of a SiO_2-Na_2O model glass batch. It has been clearly shown that quantitative information concerning the formation and evolution of intermediate reaction products can be acquired. Solid, crystalline $Na_2O•SiO_2$ is the primary reaction product of the quartz and Na_2CO_3 reaction between 700°C and 950°C. Evidence for the formation of a $Na_2O•2SiO_2$ melt at 850°C is obtained from the broad resonance peak at ~-98ppm in the ^{29}Si spectra. At temperatures greater than 1090°C the melting of crystalline $Na_2O•SiO_2$ is observed in the ^{29}Si spectra with the dramatic broadening of the resonance line.

Figure1. ^{29}Si MAS NMR spectra of a SiO_2-Na_2CO_3 glass batch heated at 10°C/min to the specified temperatures (not to scale)

Figure 2. Deconvolved ^{29}Si MAS NMR spectrum of the SiO_2-Na_2CO_3 batch heated to 850°C.

Figure 3. ^{23}Na MAS NMR spectra of a SiO_2-Na_2CO_3 glass batch heated at 10°C/min to the specified temperatures (not to scale)

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[1] Jones, A. R, Winter, R, Greaves, G. N. and Smith, I. H., J. Non-Cryst. Solids **293-295**, p. 87 (2001).

[2] Jones, A. R., Winter, R, Greaves, G. N. and Smith, I. H., Glass Technology. (In press)

[3] Meneau, F, Greaves, G. N., Winter, R and Vallis, Y, J. Non-Cryst. Solids **293-295**, p. 693 (2001).

[4] Mortuza, M. G., Dupree, R and Holland, D, J. Material Science **33**, p. 3737 (1998).

[5] Xue, X and Stebbins, J. F., Physics and Chemistry Of Minerals **20**, p. 297 (1993).

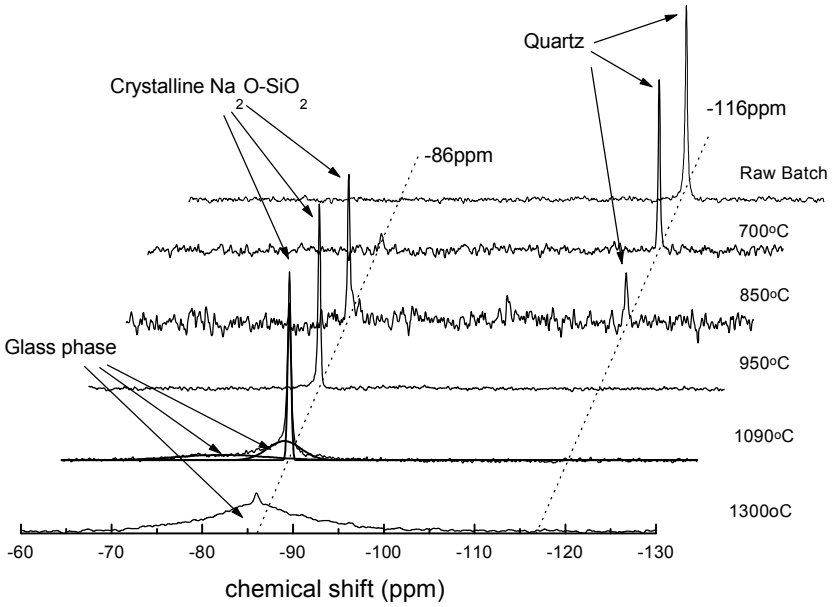

Figure 1.

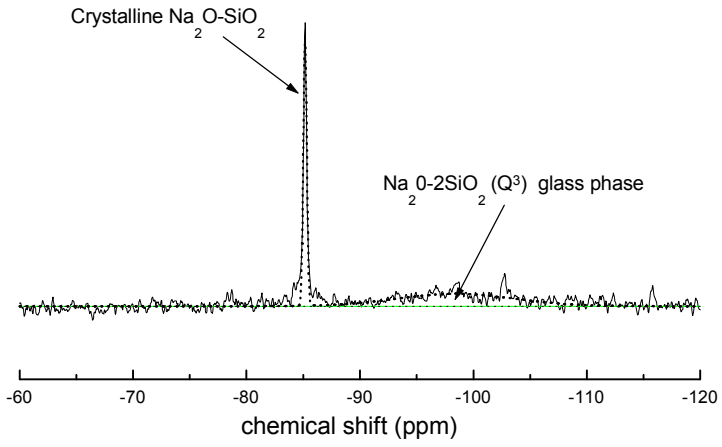

Figure 2.

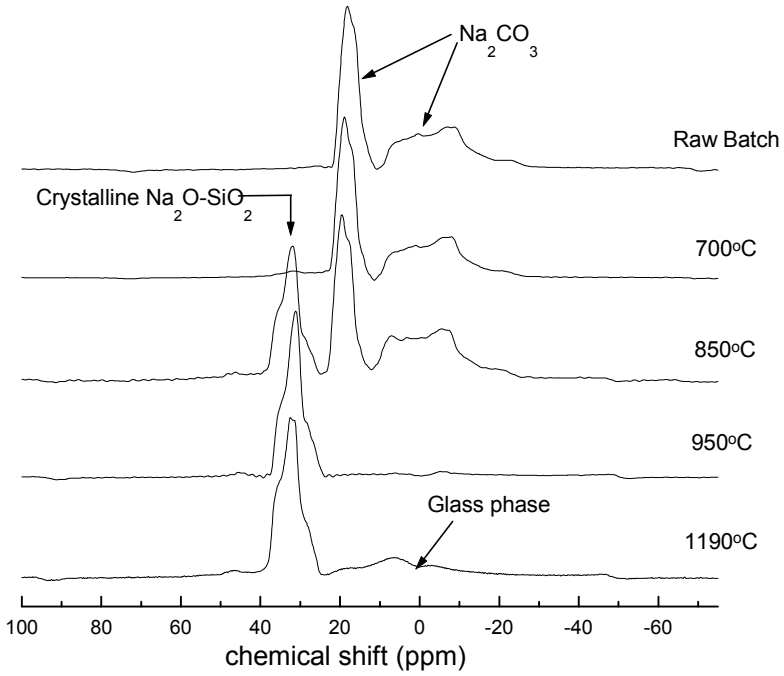
Na2CO3
Raw Batch
Crystalline Na2O-SiO2
700°C
850°C
950°C
Glass phase
1190°C
100
80
60
40
20
0
-20
-40
-60
chemical shift (ppm)

Figure 3.