Journal of Non-Crystalline Solids 505 (2019) 234–240

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Pentacoordinated and hexacoordinated silicon cations in a potassium silicate glass: Effects of pressure and temperature

Jonathan F. Stebbins*, Saurav Bista[1]

Department of Geological Sciences, Stanford University, Stanford, CA, USA

ARTICLE INFO

Keywords:
Nuclear magnetic resonance
NMR
Five coordinated silicon
Potassium tetrasilicate
High pressure
Fictive temperature

ABSTRACT

Silicon cations with five or six oxygen first neighbors (SiO_5 and SiO_6, pentacoordinated and hexacoordinated) are known primarily from alkali and alkaline earth silicate glasses melted at pressures up to about 12 GPa, where their formation is thought to be an important part of the densification of the liquid. These species, especially SiO_5 groups, have also been proposed as high-energy intermediate structures in the bond-swapping that controls network cation and anion diffusion, and hence viscous transport, in high temperature, silica-rich melts, as well as in low-temperature liquid-state silicate reactions, and have thus been the subject of numerous recent theoretical studies. In spite of this interest, the amount of experimental data on controls of pressure, temperature, and composition on concentrations of penta- and hexacoordinated silicon is very limited. Here we report new results from ^{29}Si MAS NMR on high pressure glasses with the model composition $K_2Si_4O_9$, which show that because of transient pressure drop during quench, previous studies probably significantly underestimated SiO_5 and SiO_6 concentrations. In addition, we refine the earlier results on SiO_5 even in 1 bar glasses, and demonstrate a strong increase in its concentration at higher fictive temperature. A positive enthalpy for the reaction forming this species is consistent with its role as an energetically important transition complex in melt dynamics.

1. Introduction

In nearly all crystalline silicates formed at low pressures, all Si is present in tetrahedral SiO_4 groups. Known exceptions are limited to two crystalline silicon phosphates and the calcium silicate hydrate thaumasite, in which all Si is octahedrally (hexa-)coordinated. In marked contrast, most of the Si in the deep interior of planet Earth is in SiO_6 groups, primarily in the mineral bridgmanite (perovskite-structured $[Mg,Fe]SiO_3$), which makes up most of the lower mantle at pressures greater than about 24 GPa (240 kbar) and depths greater than about 670 km. In silicate crystals, pentacoordinated silicon (SiO_5) has been observed only in a single phase, the probably-metastable triclinic polymorph of $CaSi_2O_5$ that forms at pressures of about 10 to 12 GPa [1–4].

At very high pressures, in situ X-ray scattering and other measurements on SiO_2 and other glasses suggest bond distances and densities that are consistent with complete conversion to octahedral coordination [5,6], and this is also the most likely structure for molten, multicomponent silicates in the deep Earth, perhaps at pressures above roughly 20 to 30 GPa. However, structures in liquids at intermediate pressures, which are the sources of most magmas in the modern Earth, and the effects of temperature, pressure, and composition on them, are much less well constrained because of the difficulties of detecting lesser concentrations of SiO_5 and SiO_6 by in-situ methods. Effects on physical properties such as density, viscosity, and the free energies that control phase equilibria are even less well known. Aside from the obvious effects on density of pressure-driven conversion to high-coordinated Si (densification due to closer oxygen packing), a key role for SiO_5 groups as intermediate 'transition structures' in network cation diffusion, and hence viscous flow, has long been suggested based on early molecular dynamics simulations [7–9] and on observations of anomalous viscosity decreases in some high-silica liquids with pressure [10]. The role of unusual, energetically less stable, high cation coordinations as providing insights into transition states in reaction pathways has long been appreciated in organometallic chemistry, leading to the synthesis of dozens of molecules containing pentacoordinate Si [11], including a small number containing SiO_5 groups [12,13]. Such species have also been proposed as reaction intermediates in the synthesis of zeolites [14], in aqueous silicate reactions [15], crystal nucleation [16] and even possibly in biological processes [17,18].

SiO_5 groups in silicates were first discovered by ^{29}Si MAS NMR on $K_2Si_4O_9$ glasses quenched from super-liquidus melts at the relatively

---

* Corresponding author.
E-mail addresses: stebbins@stanford.edu (J.F. Stebbins), saurav.bista@heraeus.com (S. Bista).

[1] Current address: Heraeus GMSI, LLC, Chandler, AZ, USA.

https://doi.org/10.1016/j.jnoncrysol.2018.11.001
Received 4 October 2018; Received in revised form 1 November 2018; Accepted 2 November 2018

modest pressure of 1.9 GPa [19]. SiO_6 groups were also detected, and both were seen in higher-pressure (to 12 GPa) $Na_2Si_4O_9$ and $Na_2Si_2O_5$ glasses as well [4,20–22]. The low concentrations of these species (as low as 0.2% of total Si), as well as the small size of high pressure glass samples, required in most cases the use of expensive, ^{29}Si-enriched starting materials and days-long spectroscopic experiments. These and other findings helped to reinforce a possible role for SiO_5 (and AlO_5) groups in models of viscosity and network diffusivity of high pressure liquids, despite the limited spectroscopic constraints on these structures [23–26]. Shortly after its discovery in high pressure glasses, pentacoordinate Si was detected by NMR in 1 bar glass samples of $K_2Si_4O_9$ and comparable Rb and Cs silicates [27,28]. In 1 bar glasses, SiO_6 groups, and, later, small concentrations of SiO_5 groups, were known only in compositions rich in the extremely electronegative phosphorus cation [29–32] and have been studied by advanced double resonance NMR methods [33].

In these early studies of SiO_5 groups in ambient pressure alkali tetrasilicate glasses, significant effects of cooling rate, and hence of fictive temperature (T_f), were also discovered [27,28]. The substantially lower concentrations of this species in annealed, slowly cooled glasses, when compared to those in rapidly quenched samples, suggested that SiO_5 could indeed behave as a high-energy 'transition' species (with both enthalpic and entropic drives for formation). Although it would be desirable to study high pressure samples with a range of T_f's to better constrain these connections, obtaining a suitably large span in thermal histories is experimentally difficult. Thus, data from 1 bar samples, where T_f can be better controlled and characterized, remain an important starting point for systems where high coordinated species are more abundant.

NMR on quenched (and decompressed) glasses still remains the only method that can accurately quantify the proportions of penta- and hexacoordinated silicon in glasses, at least in materials where these are subordinate species, although recent progress in in-situ, high pressure NMR is promising [34]. Most such early studies were made on glasses that were initially equilibrated at high pressure and temperatures above the liquidus (often 1000 or more °C above T_g), to ensure complete melting and to increase the probability of a completely glassy product [4,19,21,22]. Solid media high pressure apparatuses were generally used to reach high enough pressures to produce measurable structural changes, including piston-cylinder equipment (pressures to about 3 GPa) and multi-anvil 'Kawai-type' apparatus (to about 12 GPa). However, in several reports glasses were heated only to metastable equilibrium at or just above the glass transition temperature, producing in some cases substantial increases in Al and/or Si coordination [35–37]. In recent, systematic studies, focusing on more readily detectable, and much larger, pressure-induced coordination changes of B and Al cations in multicomponent glasses, we showed that the latter approach yields substantially higher (often > 50%) recoverable coordination and density increases, and concluded that this effect was the result of large, transient drops in pressure when quenching from superliquidus temperatures in solid media apparatus [38–41]. A new range of studies, primarily of multicomponent compositions of interest in problems of hardness and fracture toughness of glasses of interest in technology, have heated samples near to T_g in gas-pressurized apparatus to about 1 GPa, where changes in B and Al coordination can be large enough to be measured by NMR after quench and decompression, and effects on bulk glass properties quantified [42–44].

Pentacoordinate Si (as well as other high-energy, 'defect' sites) in silicate liquids and glasses have been the subject of a considerable number of recent molecular dynamics and other theoretical studies, many of which have focused on the role of this species in bond swapping mechanisms in cation diffusion and viscous flow [45–52]. Predicted concentrations of this species have also been used to evaluate the accuracy of models of inter-atomic potentials in such simulations. However, the very limited number of experimental studies of pressure and temperature effects on Si coordination can be a major hindrance to progress in this area.

It is clear that much more experimental data is needed on SiO_5 and SiO_6 groups in silicate glasses and liquids with simple model compositions, to better constrain their roles in pressure and temperature effects on thermodynamic and transport properties. In this report, we describe new studies of both pressure and temperature effects on the concentrations of these species in $K_2Si_4O_9$ glass, as the first part of a larger study detailing compositional effects. We show that indeed, previous results on high pressure glasses quenched from high temperature liquids probably significantly underestimated such concentrations because of pressure drop effects. In 1 bar glasses, we confirm and significantly improve measurements showing enhanced SiO_5 concentrations at higher fictive temperature. Finally, in high pressure samples that fortuitously contained minor amounts of the crystalline, high pressure form of $K_2Si_4O_9$, we find that this melts to a liquid at low temperature instead of reverting to the stable, low pressure crystal, as has been seen in the 'amorphization' of some other high pressure phases.

2. Experimental

2.1. Glass synthesis

Data presented here were collected on samples made from a single 700 mg batch of ^{29}Si-enriched $K_2Si_4O_9$ glass. This was made by mixing stoichiometric quantities of dried, high-purity K_2CO_3 (J.T. Baker 'Ultrex') and 99% ^{29}Si SiO_2 (Isonics), with 0.2 wt% Gd_2O_3 to speed nuclear spin relaxation [21], decarbonating for 12 h at 730 °C, then melting in a 3%Au Pt crucible at 1130 °C for 1 h. This was rapidly quenched by dipping the bottom of the crucible in water, resulting in an optically homogeneous, bubble-free glass that was light blue in color, possibly due to a trace of CoO that may be a contaminant in the silica starting material [53]. The glass was coarsely crushed for high pressure and NMR experiments.

2.2. High pressure experiments

Following procedures used in our recent studies of aluminosilicate and aluminoborosilicate glasses [38–41], high pressure samples were prepared using a piston cylinder (solid medium) apparatus in the U.S. Geological Survey laboratory in Menlo Park CA, with assemblies consisting of 25.4 mm diameter calcium fluoride cylinders and graphite tubular heaters. Crushed glass samples of 50 to 100 mg were welded into 5 mm Pt tubes. Most samples were heated to temperatures near to those of the ambient pressure glass transition (Table 1) to allow equilibration to the metastable liquid state but to avoid significant transient pressure drops on quench, as discussed in detail previously [38]. One experiment was done at 1.5 GPa with heating well above the liquidus temperature (to 1250 °C) to verify this effect. Samples were held at temperature for 1.5 h to allow thermal and mechanical equilibration, then quenched by cutting power to the heater.

2.3. Annealing experiments

A portion of the original, fast-quenched, 1 bar pressure glass was reheated above the glass transition (to 520 °C) for 30 min, then cooled at a fixed rate of 10 °C/h to 320 °C, to form a glass with a much lower fictive temperature. After NMR data were collected, this glass was remelted and fast quenched as for its original synthesis. As described below, glasses from runs at 3 GPa contained about 20% crystals of the high pressure "wadeite" phase of $K_2Si_4O_9$, as readily detected by NMR. One of these samples was annealed for several times and temperatures (Table 1) to explore effects of re-equilibration of these crystals at 1 bar pressure.

Table 1
Concentrations of SiO_5 and SiO_6 groups in $K_2Si_4O_9$ glass (molar % of total Si).

Pressure	Run T or cooling rate[a]	% SiO_5 ± 0.02 in glass	% SiO_6 ± 0.02 in glass	% crystals[b]
1 bar	FQ	0.1	n.d. (< 0.02)	n.d. (< 0.01)
1 bar	FQ then SC	0.05	n.d. (< 0.02)	n.d. (< 0.01)
1 bar	FQ, SC then FQ	0.1	n.d. (< 0.02)	n.d. (< 0.01)
1.5 GPa	470 °C	0.61	0.09	n.d. (< 0.01)
1.5 GPa	500 °C	0.61	0.11	n.d. (< 0.01)
1.5 GPa	1250 °C	0.22	0.03	n.d. (< 0.01)
3.0 GPa	470 °C	2.4 ± 0.1	2 ± 0.5	17
3.0 GPa	500 °C	1.8 ± 0.1	3 ± 1	19
3 GPa → 1 bar[c]	520 °C, 1 h	0.05	n.d. (< 0.02)	19
3 GPa → 1 bar[c]	520 °C, 22 h	0.06	n.d. (< 0.02)	18
3 GPa → 1 bar[c]	706 °C, 1 h, then FQ	0.1 ± 0.03	n.d. (< 0.02)	n.d. (< 0.01)

[a] Initial equilibration temperature for high pressure experiments; cooling rate from above T_g for 1 bar experiments, with FQ about 500–1000 °C/s and SC 10 °C/h.

[b] Wadeite phase of $K_2Si_4O_9$; "n.d." indicates "not detected".

[c] Initial 3 GPa, 500 °C sample, annealed at 1 bar, successively at temperatures and times listed.

2.4. NMR experiments

All ^{29}Si NMR spectra were collected at a field of 14.1T (119.14 MHz for this nuclide) with a Varian Inova spectrometer and a Varian/Chemagnetics "T3" magic angle spinning (MAS) probe with 3.2 mm zirconia rotors. For most spectra, a spinning frequency of 20 kHz with sample weights of about 30–35 mg was used; some spectra were also collected with 30% larger samples and a thin-walled rotor that limited spinning rates to 14 kHz. Simple one-pulse acquisition was used, with radiofrequency tip angles of about 30° (1 μs pulses) and pulse power levels of about 90 kHz. Frequencies were referenced to external tetramethyl silane (TMS), instrumental deadtime was 15–20 μs. Extensive study was made of nuclear spin relaxation by varying pulse delays from 0.1 to 1500 s. Most spectra shown here were chosen to provide the maximum signal-to-noise ratios (typically 1500 to 6000:1) required for accurate characterization of low concentrations of SiO_5 and SiO_6 groups, with pulse delays of 4 s and typically 10,000 to 40,000 acquisitions. These spectra are not fully relaxed, with total integrated signals about 65% of fully relaxed values, but results at longer delays give very similar results with lower precision. Data from longer-delay spectra were used to estimate crystal contents when present. Concentrations of high-coordinate Si are expressed as percentages of total Si and were derived by direct integration of the spectra with a linear baseline interpolation. These were normalized to the total intensity derived by integrating all components of the spectra, including spinning sidebands when observed.

3. Results and discussion

3.1. Pressure effects on silicon coordination

Samples from the 1 bar and 1.5 GPa experiments showed no signs of crystalline phases. As shown in Fig. 1, the central regions of the spectra containing signal from four-coordinated Si (−60 to −120 ppm) are very similar to those in several previous NMR studies of this glass composition [19,21,54,55], with broad, partially resolved contributions from SiO_4 groups with three bridging oxygens (Q^3), centered at about −94.8 ppm and from those with four bridging oxygens (Q^4) centered at about −104.2 ppm. The spectra for 1 bar and 1.5 GPa glasses are similar as well.

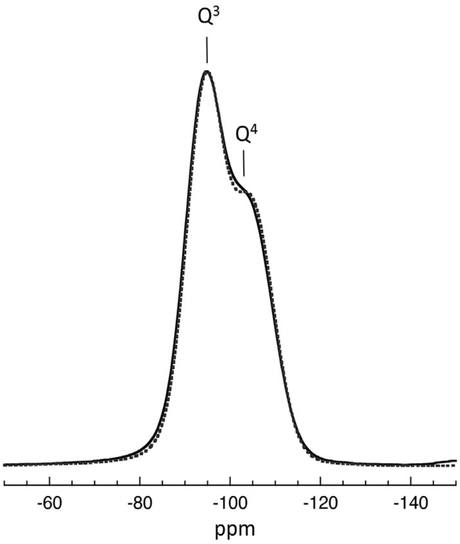

Fig. 1. ^{29}Si MAS NMR spectra of 99% ^{29}Si $K_2Si_4O_9$ glasses, showing SiO_4 region. Solid curve: quenched from 1.5 GPa, 470 °C; dashed curve: quenched from liquid at 1 bar. Here and in all except Fig. 6, spectra were collected with a sample spinning frequency of 20 kHz and spinning sidebands are absent from the frequency ranges shown.

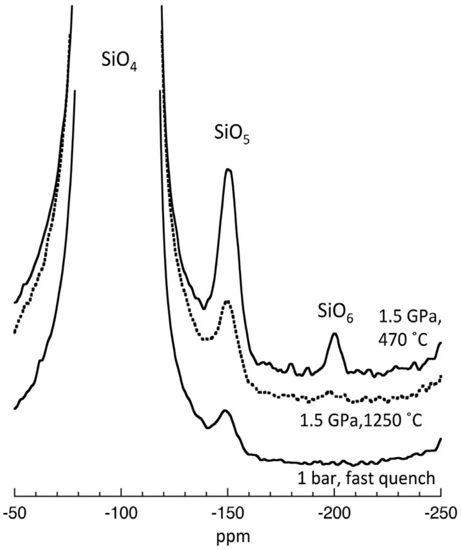

Fig. 2. ^{29}Si MAS NMR spectra of 99% ^{29}Si $K_2Si_4O_9$ glasses, including regions for SiO_4, SiO_5 and SiO_6. Vertical scale is enlarged by about x40 relative to Fig. 1. From top to bottom, spectra are for glasses quenched from 1.5 GPa, 470 °C; 1.5 GPa, 1250 °C (dashed line), and 1 bar (fast quench).

The spectra for the 1 bar and 1.5 GPa glasses also show small, broad peaks near to −149.5 ± 0.5 ppm that are now well-known to be due to SiO_5 groups [19,21]; the data for the high pressure glasses contain as well small peaks for SiO_6 groups at −200 ± 0.5 ppm (Fig. 2). The latter species is absent from the 1 bar glasses at a detection limit of about 0.02%. Concentrations of these minor species are listed in Table 1. The spectra for glasses from two different temperatures near to T_g at 1.5 GPa are nearly identical, suggesting that the run conditions allowed full relaxation to the metastable liquid structure. In marked contrast, the SiO_5 and SiO_6 contents of the sample melted above the liquidus at 1.5 GPa, then quenched, are greatly reduced. Our previous measurements of cooling rates in this high pressure apparatus demonstrated that this results not from differences in fictive temperatures but from transient pressure drops during rapid cooling of the sample and heater assembly [38].

In contrast, spectra for samples from two near-T_g temperatures at

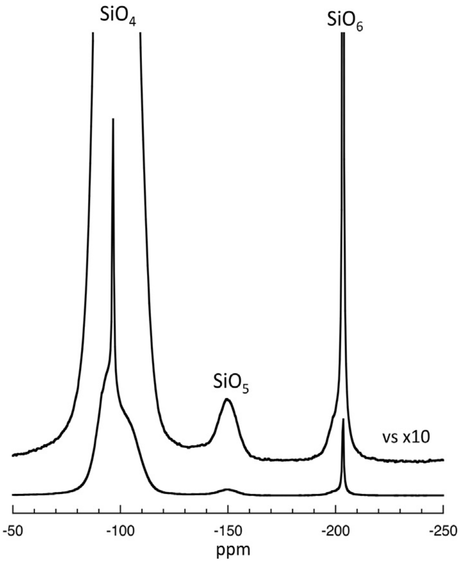

Fig. 3. ^{29}Si MAS NMR spectra of 99% ^{29}Si $K_2Si_4O_9$, quenched from 3 GPa and 470 °C. Narrow peaks in SiO_4 and SiO_6 regions are due to the crystalline $K_2Si_4O_9$ “wadeite” phase; broad components in these regions and that for SiO_5 are from the glass. Vertical scale in upper spectrum is ×10 relative to lower spectrum.

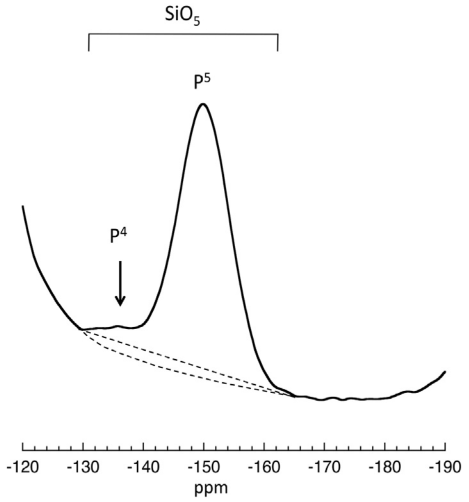

Fig. 4. ^{29}Si MAS NMR spectra of 99% ^{29}Si $K_2Si_4O_9$, quenched from 3 GPa and 500 °C, showing SiO_5 region, for data with an especially high signal-to-noise ratio (ca. 6000:1). Vertical scale is enlarged by about ×60 relative to that of the lower spectrum in Fig. 3. “P^5” labels the main component, probably due to pentacoordinate Si with 5 oxygen bridges to other Si; “P^4” labels a higher frequency component possibly due to pentacoordinate sites with 4 oxygen bridges to other Si. Dashed lines show straight baseline, as used here to integrate SiO_5 and SiO_6 peak areas (Table 1), vs. minor effect of a slightly more accurate curved baseline.

3 GPa (Fig. 3) contained, in addition to broad components for SiO_4, SiO_5, and SiO_6 groups, narrow peaks at −96.5 and −203.4 ppm known to be due to the crystalline, high pressure “wadeite” phase of $K_2Si_4O_9$, in which 1/4 of the Si cations are octahedrally coordinated and the remainder tetrahedral [56,57]. This different behavior is not unexpected: the low temperature polymorph of $K_2Si_4O_9$ (all SiO_4) is known to be slow to crystallize at 1 bar pressure and is probably stable at 1.5 GPa [58]; the “wadeite” phase becomes stable near to 2 GPa [19,59,60]. In addition, crystallization in these samples could have been accelerated if T_g is significantly reduced at 3 GPa, as expected from the known anomalous decrease in viscosity with pressure for this composition liquid [10]. In these mixed glass/crystal spectra, for the larger, SiO_4 contribution, the intensity of the glass peak can readily be estimated by simple baseline interpolation, allowing a good estimate of the total spectral intensity from the glass alone. The broad SiO_5 peak is due to the glass only; the SiO_6 glass peak is narrower and more difficult to separate from the overlapping crystal peak, increasing the uncertainty in the SiO_6 content of the glass. We estimated the area of the overlapping crystalline SiO_6 peak as 1/3 of the area of the crystalline SiO_4 peak, given the known crystal structure, and obtained the SiO_6 in the glass by difference. In Table 1, SiO_5 and SiO_6 contents for these samples are normalized to the total signal from the glass only. Because the glass and crystal have the same compositions, partial crystallization does not change the remaining glass, allowing results from these samples to be compared directly with those of crystal-free glasses. The SiO_5 content of the 3 GPa, 500 °C sample was slightly lower than that of the 470 °C sample (Table 1), suggesting a minor pressure drop during quench for the former.

Even in partially crystalline samples, the high concentration of SiO_5 in the 3 GPa glasses allows the most detailed look so far obtained at the chemical environment of this species (Fig. 4). The chemical shift of the peak maximum (−149.5 ppm) and width (FWHM of 10 ppm) are similar to those previously reported for alkali silicates [4,19,21] but are more accurate because of the higher spinning speeds, better signal-to-noise, shorter instrumental deadtime, and consequently flatter baselines than previously obtainable. This peak has generally been attributed to SiO_5 groups with five oxygen bridges to other Si, primarily because of the low network modifier content of this composition. Such species could be designated as “P^5” groups (P for “pentacoordinate,” as “Q” in “Q^n” species is derived from “quaternary”). The chemical shift of the only known SiO_5 site in crystalline silicates (in a high pressure phase of $CaSi_2O_5$ [1,3]) is at −149.5 ppm and the refined structure of this phase does indeed have this type of structural connectivity, although two of the five Si neighbors to the SiO_5 groups are octahedral instead of tetrahedral [2]. In addition, a low shoulder in the 3 GPa $K_2Si_4O_9$ data at about −138 ppm, apparently well above noise level, is consistent with the presence of a small fraction of SiO_5 groups (ca. 5 to 10%) with one non-bridging and four bridging oxygens, which could be denoted as “P^4”. Definitive assignment of this feature of the spectra will require further study of a range of compositions, however. In high pressure glasses of lower silica contents, and hence greater proportions of NBO, broad SiO_5 peaks have been reported at −143 ppm in $CaSi_2O_5$ glass from 10 GPa [3] and at −124 ppm in a 10 GPa $MgSiO_3$ glass [37]. These shifts are consistent with higher proportions of sites with one or more NBO, as this progression towards less negative values is well-known for SiO_4 groups (i.e. from Q^4 to Q^3 to Q^2 groups). A similar effect can also be seen for chemical shifts of SiO_6 groups in crystalline silicates, although the data set is much smaller [61]. Indeed, in the study of $MgSiO_3$ [37], theoretical calculations yielded a similar value for what would be denoted here as “P^3” groups, i.e. 3 BO and 2 NBO. We do not yet have other clear experimental constraints on the geometry of the SiO_5 sites, e.g. trigonal bipyramid or square pyramid, although recent theoretical calculations suggested the former [46,52]. However, the ability to observe spinning sidebands for these groups in the 3 GPa samples, with proportional intensities at a spinning speed of 20 kHz (=168 ppm) of 2–3% of the central SiO_5 glass peak, suggests a significant chemical shift anisotropy (CSA) roughly comparable to that of the SiO_4 Q^3 groups.

Fig. 5 summarizes our new results for SiO_5 and SiO_6 concentrations and compares them with data previously obtained in experiments that quenched high temperature $K_2Si_4O_9$ liquids to glasses in solid-medium high pressure apparatuses (piston-cylinder below 3 GPa, ‘multi-anvil’ at 4 GPa and above). Even without extrapolating our new data to pressures above 3 GPa, it is clear that the previous studies probably considerably underestimated the abundances of both high-coordinate species that can be recovered on decompression of high pressure liquids, presumably because of significant transient pressure drops when high

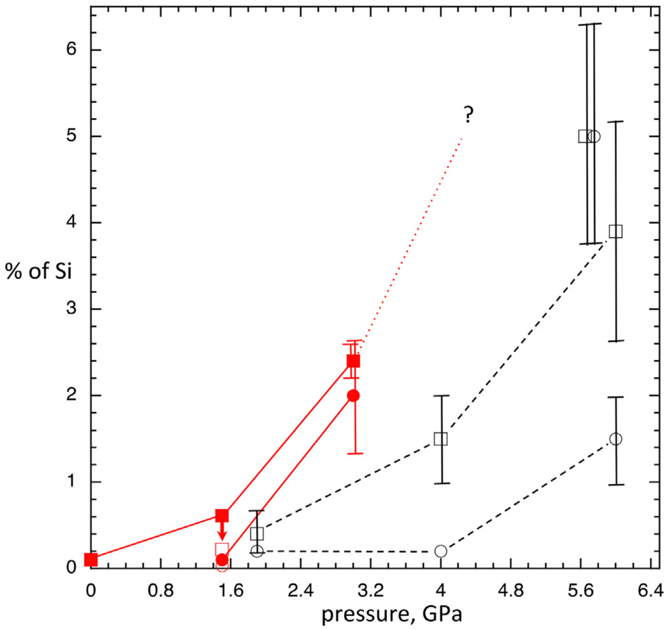

Fig. 5. Concentrations of SiO_5 and SiO_6 species (per cent, out of total Si) vs. run pressure for $K_2Si_4O_9$ glass. Squares: SiO_5; circles: SiO_6; open symbols: high run temperatures, above liquidus; closed symbols: low run temperatures, near to T_g. Red symbols and solid lines show new data presented here. Black symbols and dashed lines show data from early studies with high run temperatures: 1.9 GPa data from [19], 4 and 6 GPa data from [21], 5.7 GPa data from [4]. Arrow for new data set at 1.5 GPa shows large drop in SiO_5 from experiment near to T_g vs. from above liquidus, caused by transient pressure drop during quench of latter. Lines are to 'guide the eye' only and are not meant to represent assumed linearity of pressure effects on structure. Uncertainties are probably smaller than symbol sizes when not shown explicitly. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

initial temperatures are used. The variations among results in previous studies with high initial temperatures, especially in SiO_6 concentrations, may result from differences between different apparatus and high-pressure assemblies in the extent of this pressure drop. The limited data set suggests that the rate of increase in both high coordinate Si species may steepen at higher pressure, as was observed for the transition from AlO_4 to AlO_5 and AlO_6 groups in a number of alkali and alkaline earth aluminosilicates studied by this same approach and high pressure apparatus [38,41]. We cannot yet predict however, whether this non-linearity continues at higher pressures.

3.2. Temperature effects on silicon coordination at ambient pressure

As in our previous 1 bar pressure studies, new results for rapidly quenched $K_2Si_4O_9$ glasses show much higher concentrations of SiO_5 groups than in annealed, slowly cooled samples, by more than a factor of 2 for experiments described here (Table 1 and Fig. 6). In our previous work, we showed that these effects were reproducible and reversible by collecting spectra on an annealed sample, then fast quenching the glass, collecting further spectra, and finally re-annealing the fast quenched sample [27]. This procedure also demonstrated that the thermal history experiments did not cause changes in composition that could bias results. In the present study, we switched this procedure by initially forming a fast quenched glass, then annealing this product and cooling at a very low rate, then finally remelting and fast quenching the same sample a second time, collecting spectra at each step. Again, effects of thermal history and hence of T_f were completely reversible, and again the chance of an effect of compositional change is eliminated.

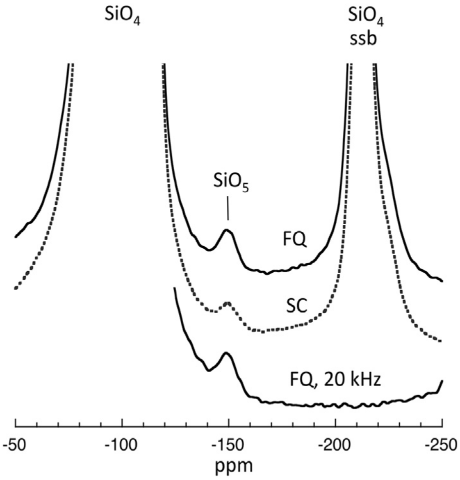

Fig. 6. ^{29}Si MAS NMR spectra of 99% ^{29}Si $K_2Si_4O_9$ glasses, quenched rapidly ("FQ") or slow-cooled ("SC") from above T_g at 1 bar. For the upper two spectra, a larger-volume sample rotor limited the spinning frequency to 14 kHz and one spinning sideband ("ssb") is present in the range plotted. This is absent from a spectrum collected with a smaller-volume rotor and a spinning speed of 20 kHz (below), which also illustrates that any signal from SiO_6 groups (expected at ca. −200 ppm) is below the noise level. Vertical scale is enlarged by about x40 relative to Fig. 1.

As discussed in several previous studies of fictive temperature effects on silicate glass structure [28,62–67], these observations have implications for the thermodynamics of equilibria among network species. It has long been pointed out that formation of SiO_5 groups in alkali silicates liquids is likely to involve the conversion of non-bridging oxygen (NBO) species, probably to oxygen anions linking SiO_4 and SiO_5 groups, with

$$SiO_4 + NBO = SiO_5 \tag{1}$$

An 'apparent' equilibrium constant for such a reaction (ignoring non-ideality and thus activity coefficients) can be written as.

$$K_{app} = X_{SiO5}/(X_{SiO4}\,X_{NBO}) \tag{2}$$

where "X's" are mole fractions of Si species out of total Si and of NBO out of total NBO. The change in speciation with T_f is manifested by a change in K_{app}, and is characterized by an apparent standard state enthalpy of reaction (ΔH_{app}) by the integrated form of the Van't Hoff equation:

$$\Delta H_{app} = -R\,[(\ln\,K_{app,Tf2} - \ln\,K_{app,Tf1})/(1/T_{f2} - 1/T_{f1})] \tag{3}$$

In the present study, available sample sizes did not permit direct measurement of T_f from differential scanning calorimetry [66]. To estimate the change in T_f in our thermal history experiments, we instead simply take T_{f1} (for the slow cooling rate of 10 K/h) as the published, annealed T_g of 773 K [68], and calculate T_{f2} for the fast quench glasses from their estimated cooling rates of 500 to 1000 K/s, yielding 930 to 940 K. The well-known dependence of T_f on cooling rate discussed previously [69,70], with the activation energy for viscosity near to T_g of 460 kJ/mol [71], and uncertainties in cooling rate, species proportions, and the viscosity curve, gives an estimated value for ΔH_{app} of 25 ± 5 kJ/mol, similar to that derived in our early study [27]. Extrapolation to temperatures far above T_f's obtainable in the laboratory is highly uncertain, but predicted SiO_5 contents may approach the percent level at 2000 K. The key issue of temperature effects on silicon coordination at high pressure remains largely unexplored by experiment.

3.3. 'Amorphization' of partially crystalline 3 GPa $K_2Si_4O_9$

The partial crystallization of both high pressure samples of $K_2Si_4O_9$ at 3 GPa provided an opportunity to study the pathways and kinetics by which both glass and crystal revert to the stable (or metastable) low pressure states on annealing at 1 bar pressure. Annealing near to T_g for 1 h caused little change in the content of the high pressure crystalline phase but reduced the SiO_5 content to the level of the 1 bar glass (Table 1). A subsequent 22 h anneal at this temperature resulted in about an 8% reduction in the signal from the high pressure crystal, but no development of the well-know group of four SiO_4 peaks characteristic of the low pressure stable crystal [56]. A final anneal for 1 h at 706 °C (followed by rapid cooling) yielded a completely amorphous glass with no crystalline NMR peaks, with a spectrum essentially identical to that of the fast quench 1 bar glass. This temperature is far above T_g but below the melting point of the stable 1 bar polymorph. This finding of metastable melting of a high pressure silicate, without crystallization to the stable 1 bar phase, is consistent with previous detailed calorimetric studies of this composition [58] and is analogous to what has been observed for the high pressure phase of silica, stishovite in which all Si is in octahedral coordination [72]. In both cases, the high pressure crystal rapidly transforms to a metastable liquid or glassy phase once a certain temperature is reached: the slow step is the crystallization of the stable, 1 bar crystalline polymorph.

4. Conclusions

New, much improved NMR data confirm that SiO_5 and SiO_6 groups can be detected in $K_2Si_4O_9$ glasses quenched from both stable and metastable melts at moderate pressures of 1.5 to 3 GPa. As has recently been found in studies of Al and B coordination changes, high (superliquidus) initial run temperatures in high pressure apparatuses can result in large transient drops in pressure during quench and significant underestimation of recoverable increases in coordination number. Samples equilibrated to the metastable liquid state just above T_g give higher concentrations of these species by largely eliminating pressure drops prior to quenching in of the structure at T_g.

SiO_5, but not SiO_6 groups are also clearly measureable in 1 bar glasses, with concentration strongly dependent on cooling rate and thus on fictive temperature, confirming and improving the accuracy of results of a small number of experiments conducted decades ago. A simple thermodynamic analysis of the formation reaction for SiO_5 yields an apparent standard state enthalpy change of 25 ± 5 kJ/mol, consistent with previous studies. The proposed role of SiO_5 as a high energy 'transition complex' in network bond swapping, diffusion, and other transport properties is thus still an interesting possibility, but may be difficult to confirm experimentally given its likely short lifetime at high temperatures. Future theoretical and simulation studies of dynamics will continue to explore the validity of this model. Experimental work on fictive temperature effects on structure at high pressure, including the ratio of SiO_5 to SiO_6 groups, could be especially important in better understanding high pressure behavior of silicate liquids in nature and in technology.

Acknowledgments

This research was supported by the U.S. National Science Foundation, grant number EAR-1521055 to JFS.

References

[1] M. Kanzaki, J.F. Stebbins, X. Xue, Characterization of the quenched high pressure phases in $CaSiO_3$ system by x-ray diffraction and ^{29}Si NMR, Geophys. Res. Lett. 18 (1991) 463.

[2] R.J. Angel, N.L. Ross, F. Seifert, T.F. Fliervoet, Structural characterization of pentacoordinate silicon in a calcium silicate, Nature 384 (1996) 441.

[3] J.F. Stebbins, B.T. Poe, Pentacoordinate silicon in high-pressure crystalline and glassy phases of calcium disilicate ($CaSi_2O_5$), Geophys. Res. Lett. 26 (1999) 2521.

[4] J.R. Allwardt, B.C. Schmidt, J.F. Stebbins, Structural mechanisms of compression and decompression in high pressure $K_2Si_4O_9$ glasses: an investigation utilizing Raman and NMR spectroscopy of high-pressure glasses and crystals, Chem. Geol. 213 (2004) 137.

[5] T. Sato, N. Funamori, Sixfold-coordinated amorphous polymorph of SiO_2 under high pressure, Phys. Lett. 101 (2008) 2555021.

[6] E.M. Stolper, T.J. Ahrens, On the nature of pressure-induced coordination changes in silicate melts and glasses, Geophys. Res. Lett. 14 (1987) 1231.

[7] C.A. Angell, P.A. Cheeseman, S. Tamaddon, Pressure enhancement of ion mobilities in liquid silicates from computer simulation studies to 800 kilobars, Science 218 (1982) 885.

[8] L.V. Woodcock, C.A. Angell, P. Cheeseman, Molecular dynamics studies of the vitreous state: simple ionic systems and silica, J. Chem. Phys. 65 (1976) 1565.

[9] S. Brawer, Relaxation in Viscous Liquids and Glasses, American Ceramic Society, Inc., Columbus, 1985.

[10] J. Dickinson Jr., C.M. Scarfe, P. McMillan, Physical properties and structure of $K_2Si_4O_9$ melt quenched from pressures up to 2.4 GPa, J. Geophys. Res. 95 (1990) 15675.

[11] H. Marsmann, In: NMR Basic Principles and Progress, Eds. P. Diehl, E. Fluck and R. Kosfeld (Berlin, Springer-Verlag, 1981) p. 65.

[12] R.R. Holmes, The stereochemistry of nucleophilic substitution at tetracoordinated silicon, Chem. Rev. 90 (1990) 17.

[13] K.C.K. Swamy, V. Chandrasekhar, J.J. Harland, J.M. Holmes, R.O. Day, R.R. Holmes, Pentacoordinate acyclic and cyclic anionic oxysilicates. A ^{29}Si NMR and X-ray structural study, J. Am. Chem. Soc. 112 (1990) 2341.

[14] B. Herreros, S.W. Carr, J. Klinowski, 5-coordinate Si compounds as intermediates in the synthesis of silicates in nonaqueous media, Science 263 (1994) 1585.

[15] J.D. Kubicki, A.C. Lasaga, Theoretical reaction pathways for the formation $[Si(OH)_5]^{1-}$ and the deprotonation of orthosilicic acid in basic solutions, Geochim. Cosmochim. Acta 57 (1993) 3847.

[16] T. Fuss, C.S. Ray, N. Kitamura, M. Makihara, D.E. Day, Pressure induced nucleation in a Li_2O-$2SiO_2$ glass, J. Non-Cryst. Solids 318 (2003) 157.

[17] S.D. Kinrade, R.J. Balec, A.S. Schach, J. Wang, C.T.G. Knight, The structure of aqueous pentaoxo silicon complexes with cis-1,2-dihydroxycyclopentane and furanoidic vicinal cis-diols, J. Chem. Soc. Dalton Trans. (2004) (2004) 3241.

[18] S.D. Kinrade, J.W. Del Nin, A.S. Schach, T.A. Sloan, K.L. Wilson, C.T.G. Knight, Stable five- and six-coordinated silicate anions in aqueous solutions, Science 285 (1999) 1542.

[19] J.F. Stebbins, P. McMillan, Five- and six- coordinated Si in $K_2Si_4O_9$ glass quenched from 1.9 GPa and 1200°C, Am. Mineral. 74 (1989) 965.

[20] X. Xue, J.F. Stebbins, M. Kanzaki, R.G. Tronnes, Silicon coordination and speciation changes in a silicate liquid at high pressures, Science 245 (1989) 962.

[21] X. Xue, J.F. Stebbins, M. Kanzaki, P.F. McMillan, B. Poe, Pressure-induced silicon coordination and tetrahedral structural changes in alkali silicate melts up to 12 GPa: NMR, Raman, and infrared spectroscopy, Am. Mineral. 76 (1991) 8.

[22] K.E. Kelsey, J.F. Stebbins, J.L. Mosenfelder, P.D. Asimow, Simultaneous aluminum, silicon, and sodium coordination changes in 6 GPa sodium aluminosilicate glasses, Am. Mineral. 94 (2009) 1205.

[23] D.C. Rubie, C.R. Ross, M.R. Carroll, S.C. Elphick, Oxygen diffusion in $Na_2Si_4O_9$ liquid up to 10 GPa and estimation of high-pressure melt viscosities, Am. Mineral. 78 (1993) 574.

[24] B.T. Poe, P.F. McMillan, D.C. Rubie, S. Chakraborty, J. Yargar, J. Diefenbacher, Silicon and oxygen self-diffusivities in silicate liquids measured to 15 gigpascals and 2800 Kelvin, Science 276 (1997) 1245.

[25] D. Tinker, C.E. Lesher, G.M. Baxter, T. Uchida, Y. Wang, High-pressure viscometry of polymerized silicate melts and limitations of the Eyring equation, Am. Mineral. 89 (2004) 1701.

[26] C. Liebske, B. Schmickler, H. Terasaki, B.T. Poe, A. Suzuki, K. Funakoshi, R. Ando, D.C. Rubie, Viscosity of peridotite liquid up to 13 GPa: Implications for magma ocean viscosities, Ear. Planet. Sci. Lett. 240 (2005) 589.

[27] J.F. Stebbins, Experimental confirmation of five-coordinated silicon in a silicate glass at 1 atmosphere pressure, Nature 351 (1991) 638.

[28] J.F. Stebbins, P. McMillan, Compositional and temperature effects on five coordinated silicon in ambient pressure silicate glasses, J. Non-Cryst. Solids 160 (1993) 116.

[29] R. Dupree, D. Holland, M.G. Mortuza, J.A. Collins, M.W.G. Lockyer, Magic angle spinning NMR of alkali phospho-alumino-silicate glasses, J. Non-Cryst. Solids 112 (1989) 111.

[30] R. Dupree, D. Holland, M.G. Mortuza, Six-coordinated silicon in glasses, Nature 328 (1987) 416.

[31] M.G. Mortuza, M.R. Ahsan, J.A. Chudek, G. Hunter, First evidence for the coexistence of four-, five- and six-coordinated silicon in glasses prepared at ambient pressure, Chem. Comm. (2000) (2000) 2055.

[32] M. Nogami, K. Miyamura, Y. Kawasaki, Y. Abe, Six-coordinated silicon in SrO-P_2O_5-SiO_2 glasses, J. Non-Cryst. Solids 211 (1997) 208.

[33] L. van Wüllen, B. Gee, L. Zuchner, M. Bertmer, H. Eckert, Connectivities and cation distributions in oxide glasses: new results from solid-state NMR, Ber. Bunsen-Gesell, Phys. Chem. 100 (1996) 1539.

[34] T. Edwards, T. Endo, J.H. Walton, S. Sen, Observation of the transition state for pressure-induced BO_3- > BO_4 conversion in glass, Science 345 (2014) 1027.

[35] J.R. Allwardt, B.T. Poe, J.F. Stebbins, The effect of fictive temperature on Al-coordination in high-pressure (10 GPa) sodium aluminosilicate glasses, Am. Mineral. 90 (2005) 1453.

[36] S.J. Gaudio, C.E. Lesher, H. Maekawa, S. Sen, Linking high-pressure structure and density of albite liquid near the glass transition, Geochim. Cosmochim. Acta 157 (2015) 28.

[37] S.J. Gaudio, S. Sen, C.E. Lesher, Pressure-induced structural changes and densification of vitreous $MgSiO_3$, Geochim. Cosmochim. Acta (2008) 1222.

[38] S. Bista, J.F. Stebbins, B. Hankins, T.W. Sisson, Aluminosilicate melts and glasses at 1 to 3 GPa: temperature and pressure effects on recovered structural and density

changes, Am. Mineral. 100 (2015) 2298.
[39] S. Bista, E. Morin, J.F. Stebbins, Response of complex networks to compression: Ca, La and Y aluminoborosilicate glasses formed from liquids at 1 to 3 GPa pressures, J. Chem. Phys. 144 (2016) 044502.
[40] S. Bista, J.F. Stebbins, The role of modifier cations in network modifier cation coordination increases with pressure in aluminosilicate glasses and melts from 1 to 3 GPa, Am. Mineral. 102 (2017) 1657.
[41] S. Bista, J.F. Stebbins, J. Wu, T.M. Gross, Structural changes in calcium aluminoborosilicate glasses recovered from pressures of 1.5 to 3.0 GPa: Interactions of two network species with coordination number increases, J. Non-Cryst. Solids 478 (2017) 50.
[42] S. Kapoor, L. Wondraczek, M.M. Smedskaer, Pressure-induced densification of oxide glasses at the glass transition, Frontiers in Materials 4 (2017) 1.
[43] M.M. Smedskaer, R.E. Youngman, S. Striepe, M. Potuzak, U. Bauer, J. Deubener, H. Behrens, J.C. Mauro, Y. Yue, Irreversibility of pressure induced boron speciation change in glass, Sci. Rep. 4 (1) (2014).
[44] M.N. Svenson, L.M. Thirion, R.E. Youngman, J.C. Mauro, M. Bauchy, S.J. Rzoka, Effects of thermal and pressure histories on the chemical strengthening of sodium aluminosilicate glass, Frontiers in Materials 3 (2016) 14.
[45] X. Yuan, A.N. Cormack, Local structures of MD-modeled vitreous silica and sodium silicate glasses, J. Non-Cryst. Solids 283 (2001) 69.
[46] J. Machacek, O. Gedeon, M. Liska, Molecular approach to the 5-coordinated silicon atoms in silicate glasses, Phys. Chem. Glasses 48 (2007) 345.
[47] J. Machacek, O. Gedeon, M. Liska, Relaxation of structural units in MD simulated silicate glasses, Phys. Chem. Glasses 47 (2006) 266.
[48] T. Ohkubo, E. Tsuchida, K. Deguchi, S. Ohki, T. Shimuzu, T. Otomo, Y. Iwadate, Insights from ab initio molecular dynamics simulations for a multicomponent oxide glass, J. Am. Ceram. Soc. 101 (2017) 1122.
[49] I. Bakk, I. Deme, D. Szieberth, L. Nyulaszi, Molecular level investigation of the dynamic structure model in molten and solid alkali glasses, Struct. Chem. 23 (2012) 1729.
[50] R.H. Doremus, Viscosity of silica, J. Appl. Phys. 92 (2002) 7619.
[51] R.H. Doremus, Transport of oxygen in silicate glasses, J. Non-Cryst. Solids 349 (2004) 242.
[52] J. Cuny, Y. Xie, C.J. Pickard, A.A. Hassanali, Ab initio quality NMR parameters in solid-state materials using a high-dimensional neural-network representation, J. Chem. Theory Comput. 12 (2016) 765.
[53] J.F. Stebbins, W.R. Panero, J.R. Smyth, D.J. Frost, Forsterite, wadsleyite, and ringwoodite (Mg_2SiO_4): ^{29}Si NMR constraints on structural disorder and effects of paramagnetic impurity ions, Am. Mineral. 94 (2009) 626.
[54] H. Maekawa, T. Maekawa, K. Kawamura, T. Yokokawa, The structural groups of alkali silicate glasses determined from ^{29}Si MAS-NMR, J. Non-Cryst. Solids 127 (1991) 53.
[55] W.J. Malfait, W.E. Halter, Y. Morizet, B.H. Meier, R. Verel, Structural control on bulk melt properties: Single and double quantum ^{29}Si NMR spectroscopy on alkali-silicate glasses, Geochim. Cosmochim. Acta 71 (2007) 6002.
[56] M. Kanzaki, J.F. Stebbins, X. Xue, Y. Syono, M.H. Manghnani (Eds.), High Pressure Research: Applications to Earth and Planetary Sciences, Terra Scientific Publishing Co., Tokyo, 1992, p. 89.
[57] D.K. Swanson, C.T. Prewitt, The crystal structure of $K_2Si^{VI}Si_3{}^{IV}O_9$, Am. Mineral. 68 (1983) 581.
[58] K. Geisinger, N.L. Ross, P. McMillan, A. Navrotsky, $K_2Si_4O_9$: energetics and vibrational spectra of glass, sheet silicate, and wadeite-type phases, Am. Mineral. 72 (1987) 984.
[59] N. Kinomura, S. Kume, M. Koizumi, Synthesis of $K_2Si_4O_9$ with silicon in 4- and 6-coordination, Min. Mag. 40 (1975) 401.
[60] M. Kanzaki, X. Xue, J.F. Stebbins, Phase relations in Na_2O-SiO_2 and $K_2Si_4O_9$ systems up to 14 GPa and ^{29}Si NMR study of the new high-pressure phases: implications to the structure of high-pressure silicate glasses, Phys. Earth Planet. Int. 107 (1998) 9.
[61] J.F. Stebbins, M. Kanzaki, Local structure and chemical shifts for six-coordinated silicon in high pressure mantle phases, Science 251 (1990) 294.
[62] J.F. Stebbins, S.E. Ellsworth, Temperature effects on structure and dynamics in borate and borosilicate liquids: high-resolution and high-temperature NMR results, J. Am. Ceram. Soc. 79 (1996) 2247.
[63] M.E. Brandriss, J.F. Stebbins, Effects of temperature on the structures of silicate liquids: ^{29}Si NMR results, Geochim. Cosmochim. Acta 52 (1988) 2659.
[64] T.J. Kiczenski, J.F. Stebbins, The effect of fictive temperature on the structural environment of fluorine in silicate and aluminosilicate glasses, J. Am. Ceram. Soc. 89 (2006) 57.
[65] E.V. Dubinsky, J.F. Stebbins, Quench rate and temperature effects on framework ordering in aluminosilicate melts, Am. Mineral. 91 (2006) 753.
[66] J. Wu, J.F. Stebbins, Quench rate and temperature effects on boron coordination in aluminoborosilicate melts, J. Non-Cryst. Solids 356 (2010) 2097.
[67] J. Wu, J.F. Stebbins, Temperature and modifier cation field strength effects on aluminoborosilicate glass network structure, J. Non-Cryst. Solids 362 (2013) 73.
[68] J.E. Shelby, Thermal expansion of mixed-alkali silicate glasses, J. Appl. Phys. 47 (1976) 4489.
[69] C.T. Moynihan, A.J. Easteal, M.A. Debolt, J. Tucker, Dependence of the fictive temperature of glass on cooling rate, J. Am. Ceram. Soc. 59 (1976) 12.
[70] T.J. Kiczenski, L.-S. Du, J.F. Stebbins, The effect of fictive temperature on the structure of E-glass: a multinuclear NMR study, J. Non-Cryst. Solids 351 (2005) 3571.
[71] I. Farnan, J.F. Stebbins, The nature of the glass transition in a silica-rich oxide melt, Science 265 (1994) 1206.
[72] X. Xue, J.F. Stebbins, A ^{29}Si MAS NMR study of sub-Tg amorphization of stishovite at ambient pressure, Phys. Chem. Minerals 19 (1993) 480.