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A High Temperature(1200 °C) Probe for NMR Experiments and Its Application to Silicate Melts

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A high temperature NMR probe was developed and applied to the measurement of ^{29}Si nucleus in sodium silicate glasses and melts. The highest temperature attained was 1200 °C. The observed ^{29}Si NMR spectra show narrowing above the glass transition temperature, due to the increase of the rate for exchange reaction among various structural species constructing the network structure.

It is well known that the NMR spectroscopy provides useful information on structures and dynamics of liquids and solids. However, ordinary NMR apparatus is applicable only for measurements up to 500 °C. In the present paper, we describe a new type probe suitable for NMR spectrometer with ppm resolution over 1200 °C. One of the important applications of the high temperature NMR is the study of silicates which are components of magmas, glasses or ceramics. The purpose of this work is to solve some technical problems associated with high temperature experiments for NMR in order to observe the temperature variation of ^{29}Si NMR spectra for silicates in the glassy and molten states in which the structure and dynamic properties are not yet well known.[1] Recently, Stebbins et al. developed a high temperature and ppm resolution NMR apparatus and applied it to silicate melts.[2] In their apparatus, samples were rapidly shuttled between a furnace and a radio frequency(rf) coil which was kept cool by a rapid flow of air in order to avoid thermal and electric disturbances from the furnace. More recently, they used a new probe for relaxation measurement which was furnished with a heater at the center of the magnet, although the detail has not been described.[3] Coutures et al. reported a laser heated high temperature probe operated over 1000 °C, and applied it to the study of molten salts.[4] In the present work, we set two heating units on the upper and lower sides of the center of the magnet.[5,6]

Figure 1 (a) shows the details of our high temperature probe. Platinum wire (0.4 mmϕ) threaded through two-hole tube (3.0 mmϕ) of high purity alumina surrounds a core alumina tube (15 mmϕ) except for the zone of center of the rf coil made of 1.0 mmϕ platinum wire. The heater current flows through two platinum wires in the same alumina tube opposite in direction so as not to produce an additional magnetic field across the sample volume. Condensers of the tuning circuit were thermally insulated with a copper pipe cooled by water. The whole assembly of the high

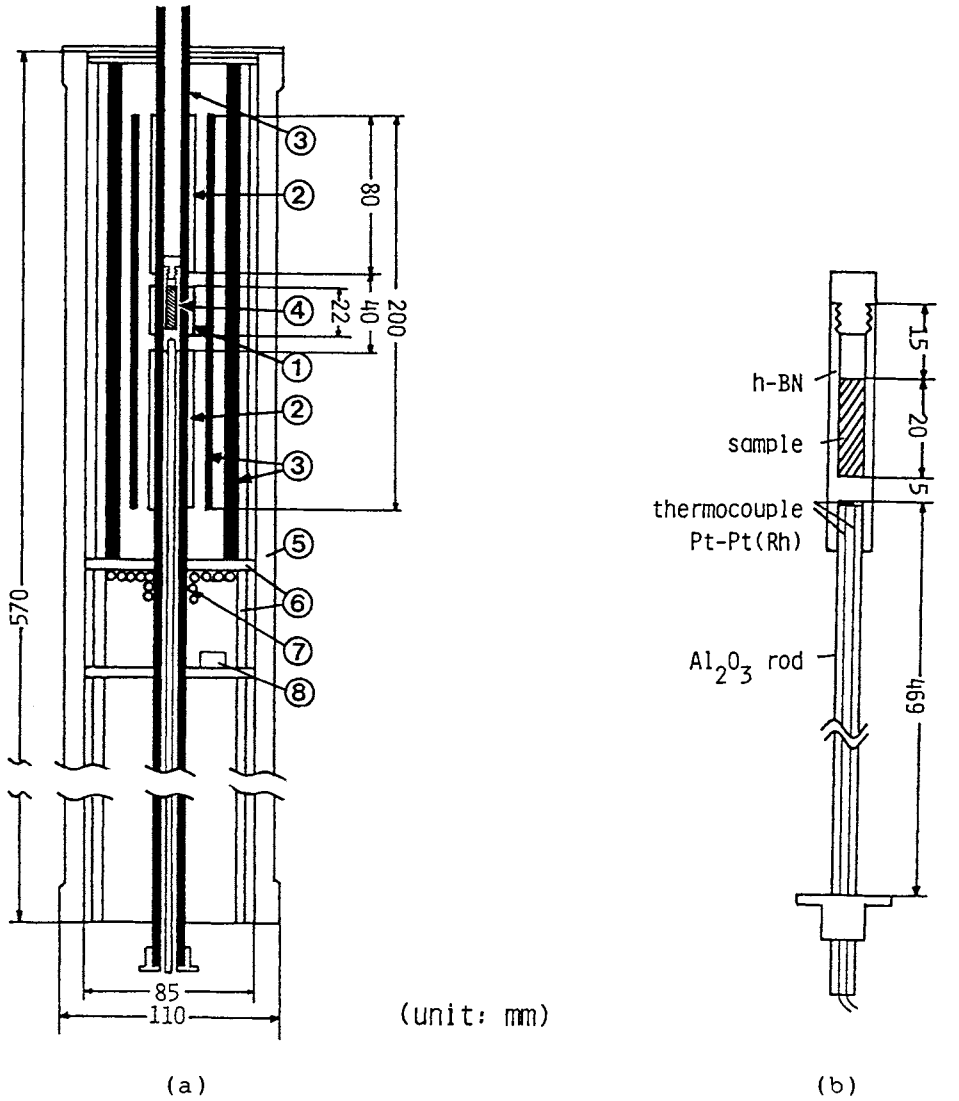

Fig. 1. (a) Schematic representation of the high temperature NMR probe. 1:rf coil, 2:platinum heater (0.4 mmϕ), 3:Al_2O_3 tube, 4:h-BN sample holder, 5:Cu-brass water jacket, 6:Ti-Al alloy (KS-130AV) stand, 7:copper pipe water cooler, 8:tuning circuit. (b) Cross section of the sample holder.

temperature probe loaded in a water jacket made of copper and brass was inserted in the superconducting magnet. During experimental runs, the condition of the furnace was monitored by a mirror placed on the upper part of the magnet. The electrical power was supplied from a stabilized dc power unit. The heater current and the applied voltage was 20 A and 40 V, respectively at the maximum furnace temperature of 1450 °C. The maximum temperature was attained in two hours. The sample capsule made of boron nitride (Fig. 1 (b)) was placed in the center of the rf coil(non-spinning). In order to avoid the oxidation of the capsule, nitrogen gas atmosphere was maintained during experiments. Sample temperature was measured by a Pt-Pt(Rh) thermocouple attached below the bottom of the capsule. The sample temperature was 1200 °C when the center of the furnace was 1450 °C. No drift of magnetic field was

found during heating and cooling cycles. However, the quality factor of the rf coil decreased considerably above 800 °C because of increase of its resistance. ^{29}Si spectra were recorded at 39.76 MHz using a Bruker MSL-200 wide bore (4.7 T, 150 mmϕ) spectrometer. The pulse width of 50 μs and repetition time of 1 to 5 seconds were used. To achieve sufficiently high S/N ratio, 2000 FID's were accumulated. Samples of natural isotope abundance were used. A small amount of paramagnetic species (0.1% Fe_2O_3) was added to reduce the relaxation time of the ^{29}Si nucleus. The observed line-width at a half height of silicate melts and that of tetraethylorthosilicate, the secondary standard of chemical shift at room temperature, was 100 Hz and 40 Hz, respectively.

The basic structural units of the silicate framework are SiO_4 tetrahedra which link together by sharing the oxygen atoms at their vertices. The resulting configurations can be classified by their topology and are denoted by Q_n. The subscript n indicates the connectivity; i.e., the number of other SiO_4 units linked to the SiO_4 tetra hedron under study. In NMR spectra of ^{29}Si, the individual peak was assigned to each Q_n species.[7] For example, the broad line ^{29}Si NMR spectrum for $Na_2O \cdot 3SiO_2$ glass (Fig. 2 (a)) consists of two components corresponding to Q_3 and Q_4 units shown by dashed and dotted lines, respectively. The Q_3 spectrum is asymmetric due to the chemical shift anisotropy. The difference of resonance frequency between Q_3 and Q_4 without chemical exchange ($\Delta\nu_0$) was derived to be 490 Hz from MAS-NMR of the same glass at room temperature. Shown in Fig.2 (b)-(e) is the temperature dependence of ^{29}Si NMR spectra of $Na_2O \cdot 3SiO_2$ glass and melt. Around 550 °C (above glass transition temperature (505 °C); presumably supercooled liquid) the line-widths of both components show narrowing. At 670 °C, the two components just overlap; i.e., the inverse of the difference of resonance frequency

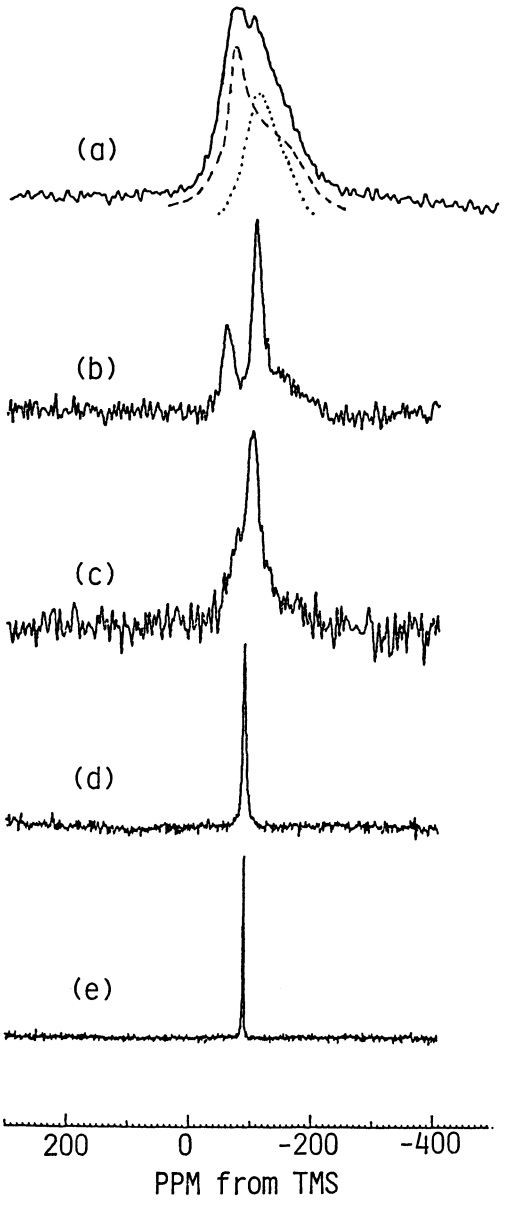

Fig. 2. Broad line ^{29}Si NMR spectra for $Na_2O \cdot 3SiO_2$ glass and liquid. (a) 20 °C, (by ordinary broad line high power NMR probe), (b) 550 °C, (c) 670 °C, (d) 770 °C, (e) 865 °C.

($\Delta\nu_0$) between Q_3 and Q_4 sites becomes comparable to the lifetime(τ) of each species. The value for τ at 670 °C was estimated to be 460 μs from the relation,

$$\tau = \frac{1}{\sqrt{2}\ \pi \cdot \Delta\nu_0} \quad .$$

Above the liquidus temperature(780 °C), a single and sharp profile of Lorentzian type was observed (Fig. 2 (e)). The line-width does not change above 865 °C up to 1150 °C, which indicates that the lifetime of each species becomes much shorter than the inverse of $\Delta\nu_0$.

The measurements of the compositional dependence of ^{29}Si high temperature NMR spectra together with the simulation for lineshapes will be discussed on a separate paper.

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