New probe for high-temperature nuclear-magnetic-resonance spectroscopy with ppm resolution

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A new type of instrument has been designed and built to make Fourier transform nuclear-magnetic-resonance (NMR) spectroscopic measurements at temperatures to at least 1200 °C, with a resolution of about 1 ppm. A sample is rapidly and repeatedly shuttled between the furnace and the radio frequency (rf) coil of the NMR probe (both located within a high field superconducting magnet), spending most of the time in the furnace. During each cycle, a series of rf pulses may be given and a single free-induction decay sampled. The rf coil is located outside of the furnace and is maintained at room temperature despite its close proximity to the sample. Electronic stability and coil "filling factor" are thus both optimized. The sample temperature drops below that of the furnace when cycling begins, but rapidly approaches a nearly constant value with only small fluctuations. 99% BN has been successfully used as a sample container in experiments on [27]Al, [29]Si, and [23]Na in molten silicates in the system $Na_2O-Al_2O_3-SiO_2$.

INTRODUCTION

Nuclear-magnetic-resonance spectroscopy (NMR) has proven to be a powerful tool for exploring the molecular structure and motion of a wide variety of solids and liquids. Recently, the application of magic angle spinning (MAS) NMR to study [29]Si, [27]Al, [23]Na, [17]O, and other nuclei in silicate crystals and glasses has provided new details of local atomic coordination and bonding in these materials.[1,2] Silicate glasses are also often used as static models for the structure of the corresponding melts. To test this assumed relationship, however, and to understand the *energetics* of the molten silicates, observations of molecular and atomic motion in the liquid state itself must also be made. As in other highly structured liquids (such as organic polymers), energetically important motions occur on time scales much slower, and on length scales much greater, than those that are directly detectable by techniques such as vibrational spectroscopy. NMR spectroscopy is one of the few methods by which such motions can be studied, and thus may provide unique and fundamental data on these materials. The particular experimental problems associated with molten silicates led us to design a new type of high-temperature NMR probe, which may prove useful in other types of chemical systems as well. The first measurements made with the instrument have been published elsewhere,[3-5] but this is the first extended description of the technical details.

Most crystalline silicates melt at temperatures above 800°C, and many at much higher temperatures. (In many systems, true liquids may persist metastably down to the glass transition temperature, which may be as low as 400°C.) These high temperatures create experimental difficulties that are even more severe for NMR spectroscopy than for other techniques, because of the general size restrictions of high-field superconducting magnets and of the necessary proximity of electronic components to the sample under observation.

Nonetheless, NMR spectroscopy has been done at temperatures as high as 1700°C.[6] Two general approaches have been taken in the past: the radio frequency (rf) coil needed to excite and receive the NMR signal has been placed either outside or inside the furnace. To compare the two designs, we note the following simplified expression for the signal-to-noise ratio ψ of an NMR experiment[7,8]:

$$\psi = cV_s T^{-1/2}\rho^{-1/4}V_c^{-\alpha},$$

where c is a factor that depends on the nucleus being studied, the magnetic field, sample temperature, coil geometry, and the characteristics of the detection circuit; V_s is the sample volume; T is the temperature of the rf coil; ρ is the resistivity of the coil material at T; V_c is the coil volume; and α has been estimated as $\frac{1}{3}$ or $\frac{1}{4}$. The rf coil may be made of a refractory metal much less conductive than copper, and its resistance may increase rapidly with temperature. In the first approach, the rf coil is kept at low temperature, surrounding the furnace, its thermal insulation, and the sample container.[9-11] This ensures the electronic stability and low-noise operation of the detection system, but severely reduces the ratio of sample volume to coil volume (the "filling factor"), thus lowering signal-to-noise ratio. The space available for insulation is also generally very limited, reducing the maximum temperature obtainable. In the second approach,[6,12-15] the rf coil is placed close to the sample, inside of the furnace. While this design increases the filling factor and the maximum sample temperature, it also necessitates the use of exotic coil materials, makes tuning difficult, and often results in relatively poor resolution.

In order to maximize the filling factor, and at the same time maintain a room-temperature rf coil for maximum resolution and sensitivity, we have designed a third alternative: the rf coil is located below the furnace and the sample is rapidly moved back and forth between the coil and the furnace.

FIG. 1. Cross section of high-temperature, high-resolution NMR apparatus. Horizontal dimensions are somewhat exaggerated for clarity, and drawing is simplified. The bore of the magnet is about 9 cm, the overall length of the apparatus is about 170 cm. (1) Water jacket plenum; (2) water jacket (double-walled type 316 stainless steel); (3) alumina sample support rod; (4) alumina tube; (5) connection to sample drive cylinder (not shown); (6) thermal insulation; (7) furnace control thermocouple; (8) furnace (vertical windings); (9) boron nitride sample container; (10) rf coil on air-cooled, Teflon support; (11) water-cooled brass plate; (12) superconducting solenoid (cryogen Dewar, superinsulation, and shim coils not shown); (13) sample container in position for rf pulse; (14) tuning electronics on support plates (very schematic); (15) probe support and air supply tubes; (16) blanket gas inlet.

I. DESCRIPTION OF APPARATUS

As shown schematically in Fig. 1, the radio-frequency NMR coil, associated tuning electronics, and high-temperature furnace are all contained in a double-walled, stainless-steel water jacket, which is inserted into the 8.9-cm bore of a 4.7-T superconducting magnet. The furnace is constructed of 0.5-mm Pt wire, threaded through 20 two-hole, 8-mm-diam Al_2O_3 ceramic tubes that are arranged in a cylinder 2 cm i.d. by 15 cm long. This configuration ensures that almost all of the current in the windings flows parallel to the axis of the solenoid, thus minimizing the force exerted on the wire by the magnetic field. A dc power supply is used to eliminate fluctuations in any residual force and the accompanying mechanical vibrations. Layers of alumina paper totaling about 2 cm in thickness surround the furnace windings, and about 5 cm of alumina-silica fiber board insulate the upper and lower ends. The electrical power required by the furnace is only about several hundred watts. A 1.4-cm-i.d. alumina ceramic tube runs the entire length of the probe and water jacket, constraining the motion of the sample container and allowing an inert or reducing atmosphere (generally Ar–$4\%H_2$) to be maintained around it.

The sample container (Fig. 2) is shuttled 15 cm between the furnace and the rf coil by an alumina rod attached to a pneumatically driven piston mounted on top of the instrument. Samples were prepared by first casting glass or crystalline cylinders in graphite molds. These cylinders could then be loaded into sample containers with a minimum of free space. Motion of the liquid (and separation into droplets)

during shuttling was thereby reduced.

In its lower position, the sample is at the point of maximum magnetic field in the superconducting solenoid; in its upper position the field is somewhat lower. During each cycle, which is synchronized with rf pulse generation and data collection by the spectrometer computer, the sample rests in the furnace for 10 s, spends about 0.2 s moving down into the rf coil, remains there for 0.1 to 0.5 s, then returns to the furnace in about 0.2 s. One or more rf pulses are given during
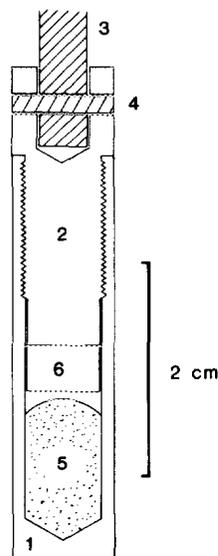
FIG. 2. Cross section of sample container. (1) Boron nitride (BN) sample tube; (2) BN top plug; (3) alumina support rod; (4) alumina pin; (5) glass cylinder as cast in graphite mold; (6) BN spacer, adjusted to sample size.

each cycle, and a single free-induction decay (FID) is recorded. 90° pulse times of about 20 μs and a 100 W broadband transmitter were generally used. Between 20 and 400 FID's are averaged together before Fourier transformation into the NMR spectrum, although rough spectra can be obtained for [23] Na with a single pulse. For [29] Si NMR on melts, the use of isotopically enriched samples is necessary. The furnace is turned off during data collection to eliminate effects of extraneous magnetic fields and electronic interference. The general principle of sample shuttling is based on the design of a probe for zero-field NMR spectroscopy.[16,17]

The rf coil itself is wound of copper wire in a two-turn Helmholtz pattern on a Teflon bar, which is kept cool by a rapid flow of air directed against the central ceramic tube. Fixed and remotely adjustable capacitors for tuning and matching the rf circuit are mounted beneath the coil. The electronic circuit is that of a standard single tuned NMR probe, adjustable to the Larmor frequencies of several different nuclei.[18]

Frequency calibration of the probe was easily done for [23] Na and [27] Al by replacing the BN sample container with a Teflon tube containing a standard aqueous solution of NaCl or $Al(NO_3)_3$. For [29] Si, however, the unavailability of an isotopically enriched standard made it difficult to calibrate the observed resonant frequencies for this nucleus. We therefore measured the frequency for [1] H in TMS (tetramethylsilane) with the high-temperature probe (at room temperature), and used a [29] Si/[1] H frequency ratio from published tables[19] to calculate the value for [29] Si in TMS for our probe. [29] Si chemical shifts (δ) are referenced to this value. For this nucleus, relative values of δ are accurate to at least 1 ppm during any given experimental run, but absolute values may have errors of perhaps 5 ppm.

Data on solid and molten NaCl indicate that there is no significant change in [23] Na chemical shifts with temperature, from room temperature to 1000°C.

II. TEMPERATURE CALIBRATION

It was anticipated that severe thermal gradients might develop within the sample during its cycling between the hot furnace and cold rf coil. Sample temperatures could not be measured during actual NMR experiments, but tests were done which indicated that temperatures are surprisingly uniform, at least in liquid and glass samples. In one such experiment, two thermocouples were inserted into holes drilled in a quartz glass rod (substituting for the more corrosive liquid sample), that was then placed in a standard sample container. One thermocouple was located in the center, the other near to the inner capsule wall. As shown in Fig. 3, during normal sample shuttling, the temperature rapidly dropped 50 to 100°C from its initial value, but leveled out at a steady state after about 3 min, oscillating only 5–10°C during each shuttling cycle. The temperature within the sample was almost exactly the same at both thermocouples, apparently because of rapid radiative heat transfer in a nearly transparent material. Enough measurements were made to define a simple, nearly linear relationship between the furnace temperature, which is monitored during all experiments, and the
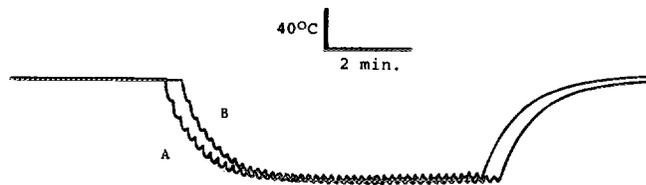
FIG. 3. Chart recording of voltages of two thermocouples during a temperature gradient test (see text). Thermocouple A was located in the center of a test sample, B within 1 mm of the capsule wall. Horizontal offset is an artifact of the recorder only: the two voltage vs time curves are essentially identical.

mean steady-state sample temperature. Temperatures during actual NMR runs could thus be calibrated. In materials that are absorptive, or in those (such as polycrystalline solids) which scatter radiation, temperature will probably be higher, but much less uniform, because of the development of conductive thermal gradients. However, it should be possible to examine areas at different temperatures in a sample by using gradient coils and NMR imaging techniques.

III. SAMPLE CONTAINER

Hexagonal boron nitride was selected as a sample container because it is an excellent dielectric, and is easily machined. Standard types of BN (made with borate binders) contaminated the alkali silicate liquid samples with CaO and B_2O_3 to an unacceptable degree, but 99% BN proved to be much better: samples contained generally less than 1–2 wt. % B_2O_3 even after 8 h at temperatures as high as 1100°C. The ease of oxidation of the BN required that a reducing or inert blanket gas be used. The use of tight-fitting,
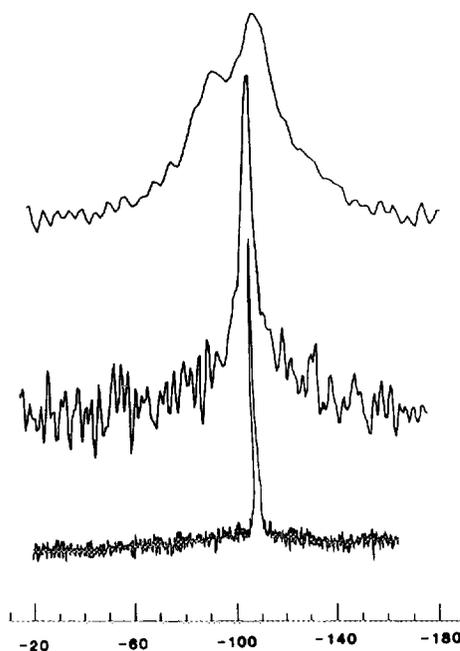
FIG. 4. High temperature [29] Si NMR spectra of $Na_2Si_4O_9$ stable and supercooled liquid. From top to bottom, sample temperatures are about 606, 695, and 828°C. Horizontal scale is chemical shift in ppm, relative to TMS. All spectra are normalized to the same maximum intensity.

threaded lids on the sample containers minimized the volatilization of alkalis from the samples that was promoted by the reducing atmosphere.

IV. EXPERIMENTAL RESULTS

As reported earlier,[3–5] we have used this new system to study ^{23}Na, ^{27}Al, and isotopically enriched ^{29}Si in melts in the system $Na_2O-Al_2O_3-SiO_2$ to temperatures of about 1100 °C. (Higher temperatures should be readily attainable.) NMR relaxation times T_1 and T_2, and chemical shifts for a number of compositions have been measured. A typical ^{29}Si spectrum is shown in Fig. 4. The peak splitting seen at the lower temperatures is probably a result of the slowing of chemical exchange between different molecular species in the melt, and of chemical shift anisotropy. (A lower quality spectrum of a liquid of similar composition was previously published.[3] The difference in the chemical shift scale of the new spectrum is the result primarily of improved frequency calibration.) Linewidths at high temperatures were as narrow as 25 Hz (0.5 ppm) for ^{23}Na in molten NaCl, and could be improved by more precise sample location and more precise field shimming (providing a more uniform and reproducible magnetic field). Future applications will include further high-temperature studies of structure and relaxation processes in melts, the nucleation of crystals from liquids, the speciation and motion of molecules on surfaces, and the observation of a wide variety of in situ reactions.

ACKNOWLEDGMENTS

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