Nuclear-magnetic-resonance study of the dynamics of network-glass-forming systems: xNa2O (1-x)B2O3

Nuclear-magnetic-resonance study of the dynamics of network-glass-forming systems: $x\mathrm{Na_2O}\cdot(1-x)\mathrm{B_2O_3}$

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The temperature dependence of the ^{11}B NMR line shapes and longitudinal-relaxation times up to 1000 °C have been investigated in glassy and liquid sodium borates with compositions $0.09\mathrm{Na_2O}\cdot0.91\mathrm{B_2O_3}$, $0.20\mathrm{Na_2O}\cdot0.80\mathrm{B_2O_3}$, $0.33\mathrm{Na_2O}\cdot0.67\mathrm{B_2O_3}$. The ^{11}B longitudinal-relaxation data are interpreted in terms of multiexponential quadrupolar relaxation, and the results are described by a reorientational correlation time τ_c. A crossover between two distinct orientational relaxation processes is observed at a temperature well above the glass-transition temperature T_g. Above the crossover temperature, the characteristics of the process are roughly similar to those of macroscopic viscosity. On the other hand, below the crossover temperature, the process is clearly distinct from that of the primary process, and is described as the secondary process. The temperature dependence of τ_c of both processes is non-Arrhenius in the temperature range studied. The value of τ_c corresponding to the secondary process is $\sim 10^{-7}$ s at T_g, and this process persists below T_g.

I. INTRODUCTION

The physical origin of the dynamic properties of glass-forming systems has been the subject of many recent investigations.[1] A number of experimental and theoretical works have been devoted to the connection between the dynamics on an atomic level and the macroscopic mechanical, dielectric, and thermal relaxation. During recent years, microscopic methods such as photon correlation spectroscopy, depolarized Rayleigh scattering, Rayleigh-Brillouin scattering, nuclear magnetic resonance (NMR), and quasielastic neutron scattering have been used to study the dynamic properties of very different glass-forming systems (ionic liquids, low-molecular-weight liquids, organic polymers, etc.).

Structural relaxation in glass-forming systems is often characterized by two separate processes: the α and β processes. In general, each process gives rise to complex dynamics of the system. The α process is extremely temperature dependent, characterized by picosecond time scales at the high-temperature limit and slowing down to time scales exceeding tens to thousands of seconds near T_g. The α process corresponds to those degrees of freedom which freeze out at the caloric glass-transition temperature T_g and is directly related to the liquid-glass transition, while the β process corresponds to those degrees of freedom which exist in both the liquid and glass. While it is believed that the β process is associated with local motions within a particular structural environment and the α process is associated with the cooperative rearrangement of this environment, the microscopic identity of the variables which are involved in these motions still remains open to controversy.

NMR has proven to be an excellent tool for obtaining detailed microscopic insights into the nature of these relaxation processes. The advantage of NMR methods is their potential in yielding information about both the α and β processes in glass-forming systems. Spiess and co-workers[2,3] have found that two-dimensional exchange Fourier-transform NMR spectroscopy monitors the α process, while the conventional NMR relaxation method probes the β process at temperatures near T_g. A number of NMR studies have been carried out with organic glass-forming systems: toluene,[4] o-terphenyl,[5] tricresylphosphate,[6] poly(vinyl methyl ether),[7] poly(vinyl acetate),[3] and polystyrene.[2] So far, however, similar work with inorganic glass-forming systems which form intermolecular networks has been somewhat neglected and limited.[8,9] This is because of the great technical difficulties encountered in performing measurements at high temperatures and the theoretical complexities in working with the structure and dynamics of the system. This often necessitates gross assumptions about the atomic motions and their relation to the measured quantities. Such difficulties can be avoided to some extent by using quadrupolar nuclei as a nuclear-spin label. Quadrupolar nuclei are very convenient probes for motional studies, since their relaxation is normally pure quadrupolar, which makes the interpretation of the relaxation data rather straightforward. In general, structural relaxation in glass-forming systems involves both translational and rotational motions. Quadrupolar interaction probes observables that depend on orientational degrees of freedom and should be sensitive to those relaxation processes which couple to molecular rotation. In contrast, experimental techniques which measure density fluctuations, such as ultrasonic relaxation and polarized light scattering, may probe structural-relaxation processes which couple more strongly to translational degrees of freedom.

Sodium borates are excellent glass formers, whose

properties have been extensively studied. The structure has also been studied by infrared and Raman spectroscopy,[10] x-ray diffraction,[11] and ambient-temperature NMR line-shape studies.[12,13] It consists of planer BO_3 triangles and BO_4 tetrahedra. These structural units are linked together by sharing the corner oxygen atoms, with randomness in orientation about the B-O bond directions. The topology of the glass network varies significantly with the sodium-to-boron ratio.[12] In pure B_2O_3 the structural unit forming the network is a planer BO_3 triangle. As sodium oxide is incorporated to the network, two competing processes that utilize the sodium cation take place. One process is the formation of BO_4 tetrahedra, and the sodium cation is located adjacent to the electrically negative BO_4 unit to provide local charge neutrality. The other process is the formation of electrically negative nonbridging oxygen atoms on a BO_3 unit coupled with an adjacent sodium cation. Below 33.3 mol % sodium oxide, the formation of nonbridging oxygen atoms is not significant and the fraction of boron atoms in BO_4 configurations increases quantitatively with increasing Na_2O content in the glass.

This paper is concerned with the ^{11}B ($S = \frac{3}{2}$) nuclear quadrupolar relaxation in sodium borates. Above the T_g region of the systems, the dominant mechanism that modulates the quadrupolar interaction at the ^{11}B site is the thermally activated random reorientational motions of the BO_3 and BO_4 units. Here the semiclassical density-operator theory of the nuclear-spin relaxation applies,[14-16] and the results can be described by a reorientational correlation time. The temperature dependence of the ^{11}B reorientational correlation time indicates a crossover between two distinct orientational-relaxation processes at a temperature well above the T_g region for all the samples. These are attributed to the α and β orientational relaxations, depending on the temperature range above and below the crossover point, respectively.

II. EXPERIMENTAL DETAILS

A. Sample preparation

The samples investigated here are of the general composition $x Na_2O \cdot (1-x) B_2O_3$ with $x = 0.09$, 0.20, and 0.33. For the preparation of the samples, mixtures of stoichiometric amounts of reagent-grade, water-free Na_2CO_3 and B_2O_3 (Nacalai Tesque Co.) were fused in Pt crucibles at 1000 °C in an atmosphere of dry N_2 for 60 min. They were then quenched, ground, and were remelted in alumina sample containers ($3 \times 3 \times 12$ mm^3) at 900 °C in an atmosphere of dry N_2 for 20 min. After being melted the samples were allowed to cool to ambient temperature. Typically, ~ 0.2 g of the sample was used in the NMR experiments. All samples were transparent and showed no sign of devitrification when checked by x-ray-diffraction techniques.

B. High-temperature apparatus

The high-temperature NMR apparatus was homebuilt and similar to that reported earlier.[17] The apparatus used here was, however, designed specifically for relaxation studies. A solenoidal Pt radio-frequency (rf) sample coil was fixed at the center of a Pt heater wound noninductively on a (CaO-stabilized) zirconia tube. The rf coil was designed to fit closely around the alumina sample containers to maximize the coil filling factor. The tuning electronics were 150 mm distant from the rf coil and could be adjusted remotely outside the magnet. The Q factor of the rf-tuning circuit was > 100 at ambient temperature, but decreased to ~ 10 at 1000 °C as a result of the increase of resistance of the rf-coil wire. The entire assembly of rf coil, sample, and heater was surrounded by thermal insulator and contained within a cylindrical water-cooled copper jacket. The latter just fit into the 120-mm magnet gap. The temperature was measured by a Pt/Pt-13% Rh thermocouple placed 3 mm below the sample. The temperature was maintained within ± 1 °C during the course of the measurements.

C. NMR measurements

The ^{11}B NMR experiments were performed with a Bruker MSL-200 pulse spectrometer operating at 64.19 MHz. The longitudinal-relaxation times were determined by measuring the longitudinal magnetization following the last pulse in $180°$-t-$90°$ sequence (inversion-recovery technique). The NMR line shapes were obtained by Fourier transforming free-induction-decay (FID) signals. A typical $90°$ pulse length is 3.8 μs at ambient temperature. Typically, 100–1000 FID signals were accumulated for each spectrum. During the course of the measurements, dry N_2 gas was made to flow through the apparatus to avoid water contamination of the sample. The ambient-temperature line shapes after the high-temperature experiments were practically identical with those of the starting material, indicating that compositional changes were insignificant.

III. THEORY

The ^{11}B ($S = \frac{3}{2}$) spin relaxation in borate glasses and liquids is driven by the coupling of the nuclear quadrupole moment $Q = 3.56 \times 10^{-2}$ (10^{-24} cm^2) with fluctuating electric-field gradients (EFG's) q present at the position of the nucleus. Above the T_g region, the dominant mechanism that modulates the EFG at the ^{11}B site is the thermally activated random reorientational motions of the BO_3 and BO_4 units. It has long been established that both the longitudinal and transverse spin relaxations produced by a quadrupole interaction are single-exponential decays if the nucleus has spin quantum number $S = 1$ or if the extreme narrowing approximation is fulfilled, i.e., if the correlation time is much shorter than the inverse of the Larmor frequency.[16,18] If neither of the conditions is satisfied, both the longitudinal and transverse relaxations produced by a quadrupole interaction are multiexponential and each is the sum of $S + \frac{1}{2}$ decaying exponentials if S is half an odd integer.

Both the longitudinal and transverse relaxations for a nuclear quadrupole Hamiltonian of a spin $\frac{3}{2}$, in a high

magnetic field, for the case of isotropic rotational diffusion are the sums of two decaying exponentials. If longitudinal relaxation is measured by the inversion-recovery technique, the recovery of the longitudinal magnetization is[16]

$$\langle S_z \rangle - \langle S_z \rangle^T$$
$$= -2\langle S_z \rangle^T [\tfrac{4}{5}\exp(-a_1 t) + \tfrac{1}{5}\exp(-a_2 t)] , \quad (1)$$

where

$$a_1 = 2CJ_2 , \quad a_2 = 2CJ_1 , \quad (2)$$

and $\langle S_z \rangle^T$ is the thermal equilibrium value of $\langle S_z \rangle$.

The real part of the spectral densities for a Debye process is

$$J_n = \tau_c (1 + n^2 \omega_0^2 \tau_c^2)^{-1} , \quad (3)$$

where ω_0 is the Larmor frequency, τ_c is the correlation time, and the constant for $S = \tfrac{3}{2}$ is

$$C = \tfrac{1}{20}(e^2 qQ/\hbar)^2 . \quad (4)$$

Here $e^2 qQ/\hbar$ is an effective quadrupole-coupling constant. The interaction parameters q and Q are the principal components of the EFG tensor and nuclear quadrupole moment, respectively.

The transverse relaxation following the 90° pulse is given by[16,19,20]

$$\langle S_x \rangle + i \langle S_y \rangle = \langle S_z \rangle^T i \exp[-i\omega_0(t - t_0)]$$
$$\times [\tfrac{3}{5}\exp(-b_1 t) + \tfrac{2}{5}\exp(-b_2 t)] , \quad (5)$$

where

$$b_1 = C(J_0 + J_1 + iQ_1) \quad (6a)$$

and

$$b_2 = C(J_1 + J_2 - iQ_1 + iQ_2) . \quad (6b)$$

The imaginary components of the spectral density,

$$Q_n = n\omega_0 \tau_c^2 (1 + n^2 \omega_0^2 \tau_c^2)^{-1} , \quad (7)$$

induce hyperfine second-order dynamic quadrupolar shifts which cause a displacement of the satellite pairs and the central line relative to each other. The Fourier transforms of the transverse-relaxation function [i.e., Eq. (5)], each of which consists of a superposition of two Lorentzians, are shown in Fig. 1 as a function of $\omega_0 \tau_c$.

IV. RESULTS AND ANALYSIS

A. Determination of ¹¹B longitudinal-relaxation times and ¹¹B quadrupole-coupling constant

According to Eq. (1), the ¹¹B longitudinal relaxation exhibits a multiexponential relaxation caused by the superposition of two exponentially relaxing components. In fact, a nonexponential recovery of the longitudinal magnetization is observed. To extract the two longitudinal-relaxation times a_1^{-1} and a_2^{-1}, it is necessary to fit the theoretical function $\langle S_z \rangle - \langle S_z \rangle^T$ to the experimental data. The least-squares fits have been carried out to determine two longitudinal-relaxation times. The logarithm of the two ¹¹B longitudinal-relaxation times a_1^{-1} and a_2^{-1} in $0.33Na_2O \cdot 0.67B_2O_3$ is shown in Fig. 2 as a function of reciprocal temperature. A definite minimum for a_1^{-1} and a_2^{-1} is observed. Also, the same features are found for other samples.
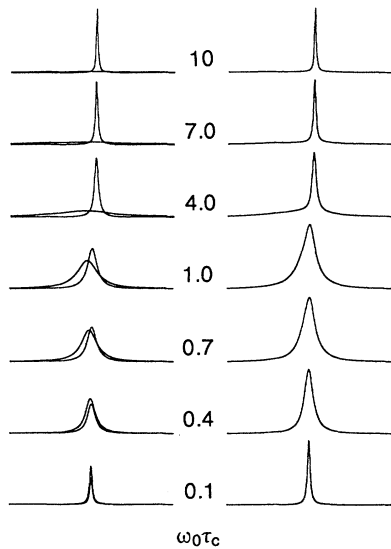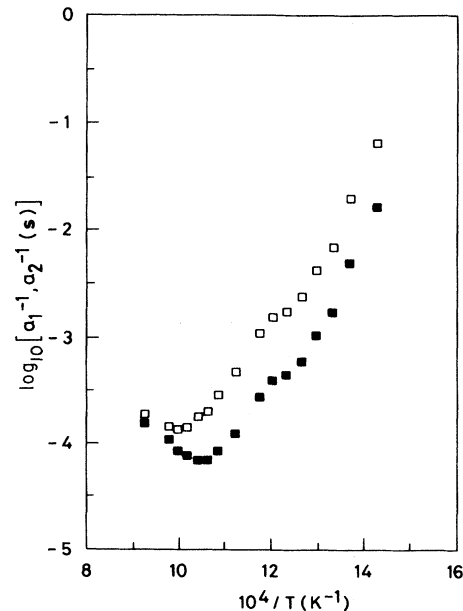

FIG. 1. Fourier transforms of the function $\langle S_x \rangle + i \langle S_y \rangle$ of Eq. (5) describing transverse relaxation (right). The spectra consist of a superposition of two Lorenzians (left). For small $\omega_0 \tau_c$ (extreme narrowing limit), the two components become identical, while in the other limit ($\omega_0 \tau_c \gg 1$) the broad component becomes so broad as to be invisible.

FIG. 2. ¹¹B longitudinal-relaxation times a_1^{-1} (open squares) and a_2^{-1} (solid squares) vs reciprocal temperature $10\,000/T$ for $0.33Na_2O \cdot 0.67B_2O_3$.
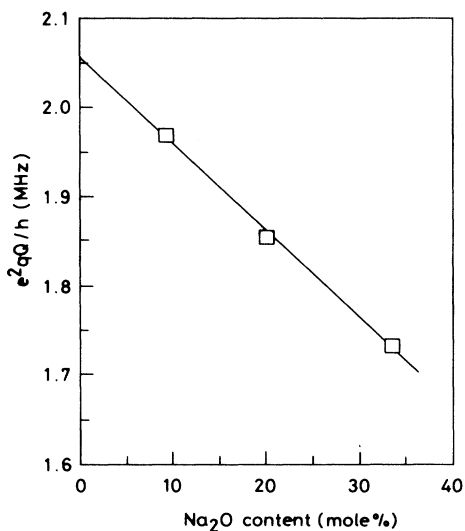
FIG. 3. Compositional dependence of the ^{11}B effective quadrupole-coupling constant determined by the longitudinal data.

20kHz

FIG. 4. ^{11}B line shapes for $0.09Na_2O \cdot 0.91B_2O_3$ (left) and calculated line shapes using the parameters of the longitudinal data (right).

According to Eq. (3), a_1^{-1} and a_2^{-1} have a minimum value when $\omega_0\tau_c = 0.7071$ and 1, respectively. From the magnitude of a_1^{-1} and a_2^{-1} at the minimum and using Eqs. (2) and (3), the effective quadrupole-coupling constant e^2qQ/h is calculated. In Fig. 3 the compositional dependence of e^2qQ/h is plotted as a function of the Na_2O content. The value of e^2qQ/h decreases with increasing Na_2O content.

B. Temperature dependence of ^{11}B correlation time

The ^{11}B reorientational correlation times have been determined from the longitudinal-relaxation data, and using these correlation times, ^{11}B spectra have been calculated by Fourier transforming the transverse-relaxation function $\langle S_x \rangle + i \langle S_y \rangle$. In Fig. 4 the calculated and experimental ^{11}B spectra are presented. A reasonable fit suggests that the Debye process of Eq. (3) seems to satisfactorily explain the experimental results. In NMR relaxation studies of low-molecular-weight liquids, Rössler and co-workers[4-6] have found that their relaxation data cannot be described by single-exponential correlation functions. They have used the asymmetric Cole-Davidson distribution of correlation times with a temperature-independent width parameter to describe the non-Debye relaxation in these liquids. Further, a non-Debye frequency behavior was also reported with organic polymers.[2,7] In contrast to their results, the deviation from the Debye process seems to be considerably small in the sodium borate systems.

The logarithms of the ^{11}B reorientational correlation time τ_c for each sample are shown in Fig. 5 as a function of reciprocal temperature. It is clearly demonstrated that in all samples the temperature dependence of the correlation time shows a bend at a temperature at which the value of the correlation time is of the order of 10^{-8} s.
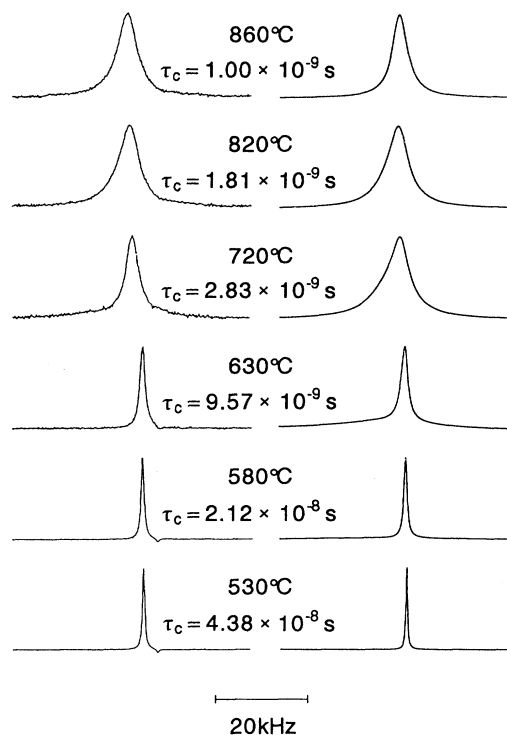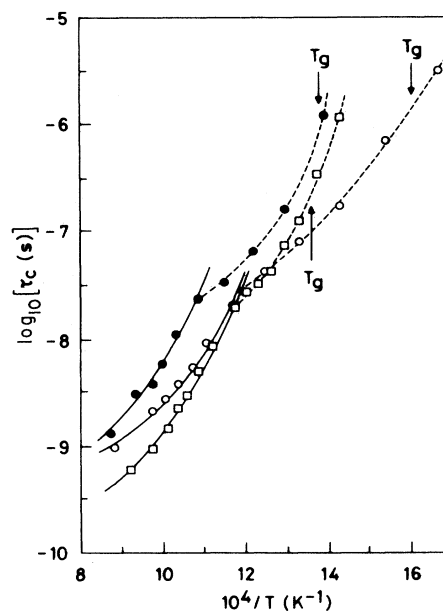

FIG. 5. ^{11}B NMR correlation times of the $xNa_2O \cdot (1-x)B_2O_3$ systems obtained from the longitudinal data: $0.09Na_2O \cdot 0.91B_2O_3$ (open circles), $0.20Na_2O \cdot 0.80B_2O_3$ (solid circles), and $0.33Na_2O \cdot 0.67B_2O_3$ (open squares). The solid lines are Vogel-Tamman-Fulcher (VTF) fits for α orientational-relaxation processes. The dashed line represents β processes.

This indicates the presence of two dynamical processes which are responsible for ^{11}B relaxation. The longitudinal relaxation on the low-temperature side of the minimum for a_1^{-1} and a_2^{-1} (i.e., $\omega_0\tau_c > 1$) is dominated by the higher-frequency motion in the range of the Larmor precession frequency. Therefore the bend in $-\log_{10}\tau_c$ vs $1/T$ plot corresponds to the crossover between the correlation times of two dynamical processes, each of which has higher frequency in the temperature region above and below the crossover temperature T_c. Both the data at high temperatures (above T_c) and at low temperatures (below T_c) show a non-Arrhenius behavior of temperature dependence. A non-Arrhenius behavior of the correlation time of the process above T_c has been previously reported for low-molecular-weight liquids[4−6] and organic polymers.[2,7] The correlation time of the process below T_c is of the order of 10^{-7} at T_g (Ref. 21) for all of the samples investigated.

V. DISCUSSION

A. Compositional dependence
of the effective quadrupolar-coupling constant

As mentioned above, the previous x-ray-diffraction work of Oh et al.,[11] infrared and Raman spectroscopy studies by Krogh-Moe,[10] and ambient-temperature NMR line-shape studies by Bray and co-workers[12,13] indicate that vitreous sodium borate consists of a random three-dimensional network of planer BO_3 triangles and BO_4 tetrahedra.

In sodium borate glasses, the boron nucleus experiences an EFG caused primarily by the electrons in the outer shell which covalently bond the boron atom to the neighboring oxygen atoms. Because of the quite different bond configurations and electron distributions for the four- and three-coordinated boron units there is a large difference in the sizes of the quadrupole-coupling constants for the two configurations. According to Bray and co-workers,[22,23] 2.4 MHz $\le e^2qQ/h \le 2.9$ MHz for BO_3 units and $e^2qQ/h \le 1$ MHz for BO_4 units.

The quadrupolar interaction shifts the NMR frequency from the Larmor precession frequency by an amount which depends on the quadrupole-coupling constant and the angle between the applied magnetic field and EFG axis. In a glass or a polycrystalline material, these angles are randomly distributed, and the resulting line shape is a powder pattern average.[24] In Fig. 6 the temperature dependence of the ^{11}B line shape for $0.33Na_2O\cdot0.67\,B_2O_3$ is shown. An ambient-temperature line shape corresponding to the rigid-lattice line shape consists of two components. A relatively narrow central line arises from the boron atoms in BO_4 units and superimposed on a broad resonance line with two characteristic peaks arising from boron atoms in BO_3 units.

As the temperature is raised, the anisotropic powder pattern sharpens into a single narrow line, owing to the thermally activated random reorientational motion which modulates the EFG at the ^{11}B site. As mentioned above, ^{11}B line shapes above $560\,°C$ are in fair agreement with the calculated line shapes using the theoretical function
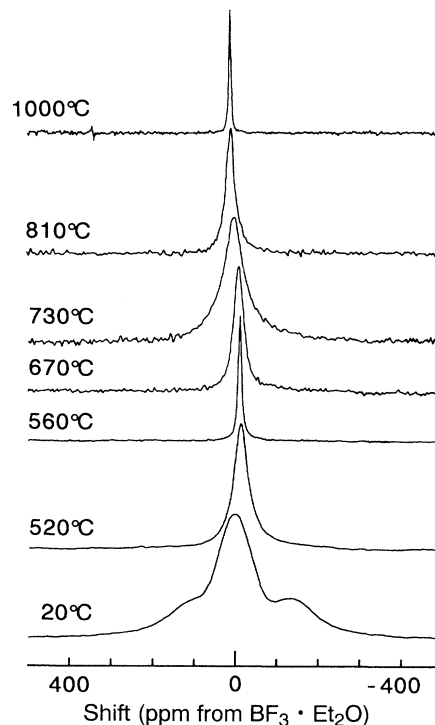

FIG. 6. Temperature variation of the ^{11}B line shape for $0.33Na_2O\cdot0.67B_2O_3$.

$\langle S_z \rangle - \langle S_z \rangle^T$. This indicates that the reorientational correlation time is much smaller than the inverse of the linewidth above this temperature. For all the samples investigated, both BO_4 and BO_3 units are thought to be present in both the glass and liquid states. However, only a single line was observed at high temperature in the liquid state. This indicates that the lifetime of boron units in the high-temperature liquid is short relative to the inverse of the difference in the NMR frequencies of BO_4 and BO_3 units. Therefore the values of e^2qQ/h determined by the longitudinal-relaxation measurements are average values which consist of contributions from both BO_4 and BO_3 units. As shown in Fig. 3, e^2qQ/h changes systematically with composition, as expected from the data on glasses. Ambient-temperature ^{11}B NMR line-shape studies have revealed that the values for the fractions of four-coordinated boron units in sodium borate systems are 0.08, 0.22, and 0.38 for $0.09Na_2O\cdot0.91B_2O_3$, $0.20Na_2O\cdot0.80B_2O_3$, and $0.33Na_2O\cdot0.67B_2O_3$, respectively.[13] The values of e^2qQ/h obtained in the present work lie between the values corresponding to four- and three-coordinated boron units and decrease as the Na_2O content increases. This result indicates that the fraction of boron units in BO_3 configurations decreases with increasing Na_2O content in the liquid state, as well as in the glass state.

B. Orientational-relaxation processes

In a network liquid such as sodium borate, structural relaxation involves both translation and rotation of the

structural units. The present probe (i.e., nuclear quadru-polar relaxation), which is sensitive to the orientational motion, should yield relaxation data on the latter. As shown in Fig. 5, nuclear quadrupolar relaxation has re-vealed two distinct orientational-relaxation processes (note that these processes are not necessarily the same as the general α and β structural-relaxation process which is measured by a probe not directly sensitive to molecular orientations): (i) an orientational-relaxation process which has the characteristics of the α process in the glass-forming system, which is roughly proportional to viscosity, and (ii) a fast process at temperatures near T_g which has not been observed before in the network-glass-forming system by NMR. This fast relaxation process at the low-temperature side is commonly referred to as the β process. Previously, the β process has been detected in low-molecular-weight liquids[5,6] and organic polymers[2] by NMR. The nuclear-spin relaxation above T_c probes the dynamics of the primary α orientational relaxation, while below T_c the nuclear-spin relaxation cannot be used to yield information on the α process. In this temperature region, the secondary β orientational relaxation governs the nuclear-spin relaxation and the correlation time cor-responds to the β process.

1. α process

The temperature dependence of the correlation times of the glass-forming systems corresponding to the α structural relaxation is usually non-Arrhenius in a certain temperature range above T_g. The degree of departure from the Arrhenius behavior leads to the strong- and fragile-liquid classification introduced by Angell[25] for which theoretical interpretations are currently being sought.[26-28] The qualitative concept of the strong and fragile liquids describes the stability of the intermediate-range order in the liquid region above T_g against a tem-perature increase. Strong liquids have overconstrained network character, which provides a reinforcement against change of intermediate-range order due to bond breaking. These liquids typically exhibit a rather slow decrease of the correlation time to the high-temperature-limit ($T^{-1}=0$) value determined by the liquid quasilat-tice vibration time ($\sim 10^{-13.5}$ s) with increasing tempera-ture. On the other hand, fragile liquids usually lack a directional character in the bonding, which leads to a high degree of configurational degeneracy. With increas-ing temperature a rapid degradation of the intermediate-range order occurs and the correlation time decreases rapidly. Consequently, the correlation time of strong liquids is usually well approximated by the Arrhenius

temperature dependence, while that of fragile liquids is better approximated by the Vogel-Tamman-Fulcher (VTF) equation, which, on the Arrhenius plot, decreases rapidly for temperatures just above T_g and exhibits a de-crease in slope at higher temperatures. The pattern of the temperature dependence of the correlation times lead-ing to this strong- and fragile-liquid classification can be reproduced by a modified version of the VTF equation in which the VTF B parameter is replaced by DT_0,[25]

$$\tau_c = A \exp[DT_0/(T-T_0)] . \tag{8}$$

Here D is the dimensionless parameter which character-izes the curvature of the Arrhenius plot, and the "strength" of the liquid goes as the parameter D. Fur-ther, this equation requires that T_g lie well above T_0 for strong liquids, whereas for highly fragile liquids T_g/T_0 approaches unity. The solid lines in Fig. 5 illustrate the fit of the correlation times corresponding to the α orien-tational relaxation to the modified VTF equation, i.e., Eq. (8). As a definition for T_g, the value $\tau_c = 100$ s is used, i.e.,

$$A = 100/\exp[DT_0/(T_g - T_0)] . \tag{9}$$

The parameters used to fit the modified VTF equation are given in Table I. VTF parameters corresponding to α structural relaxation (viscosity[29]) are also cited in the table.

D values for both α orientational and α structural re-laxation decrease with increasing Na_2O content, indicat-ing that "fragility" increases with increasing Na_2O con-tent. This compositional dependence of the fragility may be related to the difference in the skeleton structure of borate networks. The correlation between the average coordination number ($\langle r \rangle$) in covalently bonded inor-ganic glasses and the fragility has been found in the re-cent study of Tatsumisago et al.[30] ($\langle r \rangle = \sum X_r r$, where X_r is the mole fraction of atoms which have r bonds per atom). If this is applied to the present systems, the frac-tion of four-coordinated boron atoms increases with in-creasing Na_2O content, and so the average coordination number for the skeleton structure varies from $\langle r \rangle = 2.4$ (for B_2O_3) to larger values with increasing Na_2O content. The increase in fragility with increasing Na_2O content seems to be correlated with departure of the average coordination number from 2.4, the value which the minimum fragility has been found for ternary chal-cogenide systems.[30]

Although the compositional dependences of D values for both α orientational and α structural relaxation show

TABLE I. Vogel-Tamman-Fulcher (VTF) fitting parameters for NMR (α orientational relaxation) and viscosity (α structural re-laxation) results from the $x Na_2O \cdot (1-x)B_2O_3$ system. The approximate glass-transition temperature T_g for each sample is also given.

Sample x	NMR $\log_{10}(A)$ (s)	D	T_0 (K)	Viscosity $\log_{10}(A)$ (s)	D	T_0 (K)	T_g (K)
0.091	−10.4	3.4	558	−12.6	14.5	435	623
0.200	−10.3	2.5	666	−13.4	12.7	532	723
0.333	−10.2	1.3	701	−13.4	8.9	585	733

a similar trend, the D values for the former are smaller than that of the latter. This indicates that the degradation of the intermediate-range order preferentially releases the orientational degrees of freedom to a larger extent than do the translational degrees of freedom. For network liquids such as sodium borates, the α structural relaxation seems more strongly governed by translational motions.

2. β process

Nuclear-spin relaxation is capable of detecting β processes in the range of the Larmor frequency at temperatures near T_g, while two-dimensional exchange Fourier-transform NMR spectroscopy monitors a slow α process which is roughly proportional to the rapidly diverging viscosity in this temperature region.[2,3] Dielectric relaxation experiments on various glass-forming systems[31,32] and recent theoretical work on models of rotational motion in viscous liquids[33−35] suggest that between T_g and a temperature T_c well above T_g there exist a slow α orientational relaxation and a faster β orientational relax-

ation. At T_g the α orientational relaxation freezes out, and below this temperature only the β orientational relaxation persists. It is postulated that the β process is due to small-step angular motion of a molecule (or a structural unit) within a torsional well. However, the detailed molecular origin of the β process is not yet clear. The magnitude of correlation times of β processes is on the order of 10^{-7} s as can be seen in Fig. 5. Since the linewidth at ambient temperature, which corresponds to a rigid-lattice one, is about 20 kHz (see Fig. 6), the correlation times are in the fast motional limit, i.e., fast enough to change the line shape. However, the ^{11}B line shape near T_g is not modified. Hence hindered small-angle librations which do not alter the spectra may be responsible for this process.

ACKNOWLEDGMENTS

[1]See, for example, *Proceedings of the International Discussion Meeting on Relaxations in Complex Systems* [J. Non-Cryst. Solids **131-133**, (1991)].

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