Relaxation Phenomena of Ultrasonic Waves on Molten Alkali Silicates

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The temperature and the frequency dependencies of velocities and absorption coefficients of ultrasonic waves have been measured on molten alkali silicates (33(mol%)M_2O–67SiO_2 (M = Na and K)) using the pulse transmission technique. The velocities and the absorption coefficients have been determined by the Fourier transform of ultrasonic pulses. It has been found that the velocities, c, increases with decreasing temperature, while the absorption per wavelength, αλ, increases and then decreases with decreasing temperature. It has also been found that the c and αλ values are identical irrespective of frequencies above ca. 1400 K for 33Na_2O·67SiO_2 and ca. 1500 K for 33K_2O·67SiO_2, respectively, while dispersion, i.e., frequency dependency, appears below these temperatures. The dispersions of acoustic properties have been successfully interpreted using a structural relaxation model.

KEY WORDS: molten alkali silicate; ultrasonic wave; velocity; absorption coefficient; pulse transmission technique; relaxation; dispersion; bulk viscosity; longitudinal modulus; compressibility.

1. Introduction

Ultrasonic waves have potential application in refining processes. For example, the size and distribution of nonmetallic inclusions in molten steel and the thickness of refractory walls of blast furnace can be estimated by using an ultrasonic inspection meter. Velocity and absorption coefficient of ultrasonic waves also have scientific interest because they are relevant to the thermodynamic, thermophysical and mechanical properties such as adiabatic compressibility, bulk and shear viscosities and elastic modulus.

Fluids in equilibrium are always isotropic and only longitudinal waves can propagate. The ultrasonic velocity is generally independent of the frequency of waves used for the measurement at higher temperatures. If it is assumed that the propagation of ultrasonic waves proceeds adiabatically and that local fluctuation of liquid density due to the propagation of ultrasonic waves is negligibly small, adiabatic compressibility βs could be calculated from the determined velocity of ultrasonic waves c with the equation,

\[ \beta_s = \frac{1}{\rho c^2}, \]

where \( \rho \) is the density of the sample. The ultrasonic velocity generally decreases with increasing temperature as long as the coordination structure does not change. This is because thermal motion of the ions leads to an increase in the nearest-neighbor separation, resulting in an increase in compressibility. It has been reported that ultrasonic velocity decreases with temperature for molten slags and salts, and many liquid metals. Ultrasonic velocities of molten alkali silicate have been reviewed by the authors.

There are losses or absorption of acoustic energy by the medium. The absorption of acoustic energy in fluids can be described by a phase lag between acoustic pressure and the medium response (density or volume change); non-reversible process leads to the energy absorption. The absorption of acoustic energy will be associated with the frequency of waves as follows.

Acoustic pressure \( p \) could be described by the Kelvin-Voigt model as follows,

\[ p = Ms + \eta \frac{\partial s}{\partial t} = \rho c^2 s + \eta \frac{\partial s}{\partial t} \]

where \( M \) is the longitudinal modulus which is equal to \( \rho c^2 \) (see Appendix I), \( s = -\partial u / \partial x \) (\( u \) is the displacement of atoms) meaning the relative density change or condensation, and \( \eta \) is the longitudinal viscosity. The first and the second terms of the right hand side of Eq. (2) correspond to the elastic term (Hooke’s law) and the viscous term (Newton’s law of viscosity), respectively. The viscous term is relevant to the absorption. Figure 1(a) shows the Kelvin-Voigt model, where the elastic and viscous terms are illustrated by the spring and dash pot, respectively. If a step function pressure change \( \Delta p_0 \) is applied at \( t = 0 \), the solution is...
Theory of viscoelasticity. Thus, when the bulk and shear viscosities, respectively, owing to the conventional viscosity measurements, can be defined by

\[ \eta = \frac{\rho c^2}{\omega^2} \]

and if a step function pressure is suddenly removed

\[ s = \frac{\Delta \rho}{\rho c^2} \exp\left(-\frac{\rho c^2 t}{\eta}\right) \]

Therefore, a viscous relaxation time \( \tau \) can be defined by

\[ \tau = \frac{\eta}{\rho c^2} = \frac{\eta}{M} \]

On the other hand, from the equation of motion,

\[ \frac{\partial p}{\partial x} = -\rho \frac{\partial^2 u}{\partial t^2} \]

Substituting Eq. (6) into Eq. (2) yields

\[ \frac{\partial^2 u}{\partial t^2} = c^2 \frac{\partial^2 u}{\partial x^2} + \frac{\mu}{\rho} \frac{\partial^4 u}{\partial x^4} \]

The displacement of atoms \( u \) can be described by a traveling wave;

\[ u = u_0 \exp\{i(\omega t - kx)\} \]

where \( k \) is the wave vector, \( \omega \) is the angular frequency and \( u_0 \) is constant. The effects of attenuation are incorporated by using a complex wave number, \( \kappa^* = k - \alpha i \). Then,

\[ u = u_0 \exp\{i(\omega t - (k - \alpha i)x)\} = u_0 \exp\{i(\alpha t - kx)\} \]

Here, \( \alpha \) is the absorption coefficient. Substituting for \( u \) into Eq. (7) and separating real and imaginary parts

\[ \left( \frac{\alpha}{\omega} \right)^2 = \frac{1}{2c_0^2} \left[ \frac{1}{(1 + \omega^2 \tau^2)} - \frac{1}{1 + \omega^2 \tau^2} \right] \]

\[ \left( \frac{c_0}{c} \right)^2 = \frac{1}{2} \left[ \frac{1}{(1 + \omega^2 \tau^2)} + \frac{1}{1 + \omega^2 \tau^2} \right] \]

where \( c_0 \) is the velocity of ultrasonic waves for \( \omega^2 \tau^2 << 1 \). At low frequencies of \( \omega^2 \tau^2 << 1 \), Eq. (10) reduces to \( \alpha = \omega \tau^2 / 2c_0 \) by Maclaurin expansion. That is to say,

\[ \frac{\alpha}{f^2} = \frac{2\pi^2 \tau}{c_0} = \frac{2\pi^2}{c_0} \left( \frac{\eta_s + 4/3 \eta_s}{3} \right) \]

where \( f \) is the frequency, and \( \eta = \eta_s + 4/3 \eta_s (\eta_s \) and \( \eta_s \) are the bulk and shear viscosities, respectively) owing to the theory of viscoelasticity. Thus, when \( \omega^2 \tau^2 << 1 \), \( \alpha \) is independent of frequency. If \( \alpha \) is measured and \( \eta_s \) is known from conventional viscosity measurements, \( \eta_s \) can be determined by Eq. (12). Nagata et al.\(^\text{x}\) and Shiraishi et al.\(^\text{y}\) have obtained

bulk viscosities for some molten silicates using Eq. (12).

In fact, however, \( \alpha/f^2 \) depends on frequency. The velocity of ultrasonic waves, \( c \), also depends on frequency (see Eq. (11)). Such frequency dependency, which is called “dispersion”, is due to the structural relaxation and can be explained as follows: Molten silicates exhibit “the glass transition”, which corresponds to a kinetic barrier dividing the behavior of silicate melts into two types, liquid and glassy. Liquid behavior is the equilibrium response of a melt to an applied perturbation. Glassy behavior occurs when the timescale of the perturbation is too short for melt equilibriums, that is, when the time required for structural rearrangements is much longer than the timescale of our observations. The time- or frequency- dependent response of the structure and properties of a melt to a perturbation is termed “relaxation”. Relaxation occurs around the glass transition temperature. In ultrasonic studies, the observation timescale is microseconds. Hence, the “glass transition temperature” is raised by several hundred degrees above the conventional value. There are very few studies with respect to the relaxation phenomena in terms of the ultrasonic waves on molten silicates.

The aim of this study is to measure the temperature and the frequency dependencies of velocities and absorption coefficients of ultrasonic waves on molten alkali silicates so as to elucidate the relaxation phenomena of ultrasonic waves. In particular, relaxation mechanism of bulk viscosity will be discussed because the bulk viscosity can only be obtained by acoustic property measurements. To the best of the authors’ knowledge, relaxation mechanism of bulk viscosity has not been studied yet on molten silicates so far.

2. Experimental

2.1. Principle

The pulse transmission technique was employed in the present study. In this technique, pairs of buffer rods and transducers are used. Longitudinal acoustic pulses generated from the upper (or lower) transducer travel through the attached rod, the liquid, and the other rod in turn, and are received by the lower (or upper) transducer. The upper rod can be vertically shifted by a distance \( \Delta x \), which is measured very accurately by, for instance, a micro-screw gauge or a cathetometer. The time required for a pulse to travel from one transducer to another can be measured by an oscilloscope. The velocity of ultrasonic waves \( c \) can be calculated by the ratio of the distance between two ends of the rods (\( \Delta x \)) and the time required for the transmission of the ultrasonic pulses (\( \Delta t \)).

\[ c = \frac{\Delta x}{\Delta t} \]

If the amplitude of a pulse is changed from \( u_0 \) to \( u_0 e^{i\alpha x} \) after the pulse travels through the distance \( x \) in the sample, it can be expressed by

\[ u_0 = u_0 e^{i\alpha x} \exp\{i(\omega t - kx)\} \]

If the distance \( x \) is varied to \( x + \Delta x \), the amplitude is expressed as follows,

\[ u_0 + \Delta u = u_0 e^{-\alpha(x + \Delta x)} \exp\{i[(\omega t + \Delta t) - k(x + \Delta x)]\} \]
2.2. Sample Preparation

Master glasses of (mol%) 33M₂O·67SiO₂ (M = Na and K) were prepared from reagent grade SiO₂, Na₂CO₃ and K₂CO₃ powders. Powders were dried enough at elevated temperatures. Weighed mixtures of SiO₂ and carbonates were placed in platinum crucibles and melted in air for 20 min at temperatures around 1450°C. After being degassed, glassy samples were prepared from pouring the melts onto a copper plate and crushed to obtain the samples.

2.3. Apparatus

Figure 2 shows a schematic diagram of the experimental apparatus. The experimental setup consists of an alumina crucible (60 mm in outer diameter, 50 mm in inner diameter, and 50 mm in height) containing the sample and two buffer zones of the furnace. The piezoelectric transducers of BaTiO₃ crystal for acoustic pulses with the catalog frequencies of 1, 5 and 10 MHz (Olympus, Models A114S-RB, A108S-RB and A111S-RB) were fixed to the ends of the rods in line with the clamps, and glycerin was applied at the interfaces between the transducers and the rods to improve contact.

The sample was heated by a furnace with Kanthal Super heating elements and melted in air. During the course of the experiments, the temperature of the liquid sample was measured using a Pt-13%Rh/Pt thermocouple, calibrated periodically and positioned in contact with the lower part of the alumina crucible.

A pulser-receiver (Panametrics-NDT, Model 5077PR) generated electrical signals (pulse voltage 400 V, pulse repetition rate 100 Hz), which were converted to longitudinal acoustic pulses by the lower transducer. The longitudinal acoustic pulses traveling through the liquid sample were converted to electrical signals by the upper transducer, which were detected and amplified by the same pulser-receiver, and displayed on an oscilloscope (Sony Tektronix, Model TDS520D).

2.4. Procedure

After setting a sample in the furnace, the temperature was increased to the maximum measurement temperature and held at the temperature for 30 minutes. Subsequently, the sample was exposed to a vacuum for 30 minutes to help remove air bubbles contained in the sample. After degassing, the vacuum pomp was stopped and the air was introduced into the furnace. Measurements were carried out in air during the cooling cycle until the temperatures at which the samples were solidified and the upper rod could not be moved. The liquid sample was held for at least 1 hour at each measurement temperature prior to the measurement to confirm that the sample was at thermal equilibrium. The upper rod was shifted down vertically using a stepping motor so that the rod was immersed in the center of the liquid sample. Longitudinal acoustic pulses of 1, 5 and 10 MHz were generated from the lower transducer, traveled through the attached rod, the liquid, and the other rod in turn, and were detected by the upper transducer in order to measure the time required for the transmission of the acoustic pulses. Subsequently, the distance between two ends of the rods was altered by changing the position of the upper rod, where the change in the distance (Δx) was measured by a cathetometer to an uncertainty of 10 μm. The transmission times were acquired for nine to ten different distances between two ends of the rods.

3. Results

Three transducers for 1, 5 and 10 MHz pulses were used for the measurements. Figure 3 shows the wave profiles of ultrasonic pulses at Δx = 0 and 1.905 mm generated by the 5 MHz transducer. Figure 4 shows the frequency versus amplitude curves obtained by the Fourier transform of pulses in Fig. 3. The sample is 33Na₂O·67SiO₂ and the measurement temperature is 1223 K. Inspection of the frequency versus amplitude curve at Δx = 0 in Fig. 4 indicates that the frequency at which the amplitude shows the peak is not 5 MHz but 3.6 MHz. It has also been found that the frequencies of the peak amplitude for the 1 and 10 MHz transducers are actually 1.2 and 6.0 MHz, respectively. It can be seen from Fig. 3 that the wave shape is deformed after the pulse travels through the sample. The reason is that the acoustic amplitudes at higher frequencies attenuate more than those at lower frequencies, as shown in Fig. 4 (also see Eq. (12)). Consequently, in order to obtain the velocity c and the absorption coefficient α from the analysis of acoustic pulse, the pulse may have to be taken as a superposition of
waves with continuum frequencies instead of a single wave. Therefore, the values of \( c \) and \( \alpha \) have been determined using Fourier transform. The detail is described in Appendix II.

Figure 5 shows the \( c \) and \( \alpha \lambda \) values as a function of \( \log f \), where \( \lambda \) is the wavelength of ultrasonic waves. \( \alpha \lambda \) means the absorption per wavelength. Closed and open triangles are the \( c \) and \( \alpha \lambda \) values calculated using Fourier transform, and closed and open circles are the \( c \) and \( \alpha \lambda \) values obtained by the conventional method described in the section 2.1.

The error bars represent the standard deviations of nine to ten \( c \) and \( \alpha \) values measured by changing the position of the upper buffer rod nine to ten times. In this study, the standard deviations of the \( c \) and \( \alpha \) values are calculated as \( \pm \)1.5\% and \( \pm \)5.0\%, respectively. The error in the \( \alpha \lambda \) value can be calculated by taking the square root of the sum of the squared error in \( c \) and the squared error in \( \alpha \):

\[
\sigma_{\alpha \lambda} = \sqrt{\left(\frac{\sigma_c}{c}\right)^2 + \left(\frac{\sigma_\alpha}{\alpha}\right)^2}
\]

where \( \sigma_{\alpha \lambda} \), \( \sigma_c \) and \( \sigma_\alpha \) are the standard deviations of the \( \alpha \lambda \), \( c \) and \( \alpha \) values, respectively. It is seen that the \( \alpha \lambda \) values calculated by two methods are in poor agreement with each other. Since the wave shape of ultrasonic pulse is deformed after the pulse travels through the sample, as shown in Fig. 3, the \( \alpha \) values deduced from amplitudes of ultrasonic pulses (open circles) could contain large errors. This discrepancy in \( \alpha \) values demonstrates necessity of the Fourier transform of ultrasonic pulses.

Although the Fourier transform of ultrasonic pulses enables us to obtain the frequency dependency of the \( c \) and \( \alpha \) values, the \( c \) and \( \alpha \) values at 1.2, 3.6 and 6.0 MHz are only considered hereafter to avoid heavy calculations. Figures 6 and 7 show the temperature dependencies of the \( c \) and \( \alpha \lambda \) values at 1.2, 3.6 and 6.0 MHz for 33Na2O·67SiO2 and 33K2O·67SiO2, respectively. The liquidus temperatures of the samples are indicated by the dashed lines with ‘L.T.’.

The error bars represent the standard deviations of nine to ten \( c \) and \( \alpha \) values measured by changing the position of the upper buffer rod nine to ten times. The measurements for 33Na2O·67SiO2 and 33K2O·67SiO2 were carried out down to 898 K and 1113 K, respectively, which are around 200 K lower than the respective liquidus temperatures. It has been found that both samples are glassy after the experiments. Previous data are also included in Figs. 6 and 7. Their results are in agreement with the values in this study. It can be seen from Figs. 6 and 7 that the \( c \) and \( \alpha \lambda \) values are identical irrespective of frequencies above ca. 1400 K for 33Na2O·67SiO2 and ca. 1500 K for 33K2O·67SiO2, respectively, while dispersion, i.e., frequency dependency, appears below these temperatures. As aforementioned, dispersion stems from the structural relaxation of molten silicates. The relaxation phenomena of velocity and absorption coefficient of ultrasonic waves are discussed in the next section.
4. Discussion

4.1. Relaxation Model by Herzfeld and Litovitz

According to the Kelvin-Voigt model shown in Fig. 1(a), the dispersion of acoustic properties can be expressed by Eqs. (10) and (11). However, the Kelvin-Voigt model has a drawback that when the frequency becomes extremely high, the dash pot becomes rigid and the elastic deformation cannot take place, which is at odds with the truth. This can be solved by the Maxwell model. The Maxwell model assumes that a viscous dashpot with Newtonian viscosity \( \eta \) and a Hookean spring with longitudinal elastic modulus \( M \) are combined in series (see Fig. 1(b)). The Maxwell model is explained in Appendix III.

In fact, the longitudinal modulus \( M \) consists of the bulk modulus \( K \) and the shear modulus \( G \). Figure 8 shows the illustration of the strain for each elasticity modulus. As shown in Fig. 8, the bulk strain leads to volumetric change, while the shear strain does not. Herzfeld and Litovitz have proposed that the combination of the bulk modulus \( K \) and the shear modulus \( G \) can be represented by the mechanical model shown in Fig. 9. The complex bulk modulus \( K^* \) is expressed by the parallel of the zero frequency bulk modulus \( K_0 \) with the series of the bulk viscosity \( \eta \) and the relaxation part of bulk modulus \( K_2 \). The complex shear modulus \( G^* \) is described by the series of the shear viscosity \( \eta_s \) and the high-frequency shear modulus \( G_\infty \). The zero frequency bulk modulus \( K_0 \) is necessary owing to the following reason; if \( K_0 \) is not incorporated in the model, the \( K^* \) value (i.e., the resistance against volumetric change) approaches zero and...
the compressibility becomes infinite as increasing frequency.

In analogy with Eq. (A34), the $K^*$ and $G^*$ values are expressed as follows:

$$K^* = K_0 + \frac{4}{3} G^* = K_0 + \frac{K_o \omega^2 \tau_v^2}{1 + \omega^2 \tau_v^2} + \frac{(4/3) G_o \omega^2 \tau_v^2}{1 + \omega^2 \tau_v^2} + i \left( \frac{K_o \omega \tau_v}{1 + \omega^2 \tau_v^2} + \frac{(4/3) G_o \omega \tau_v}{1 + \omega^2 \tau_v^2} \right) \quad \ldots \ldots (20)$$

$$G^* = G_o \omega^2 \tau_v^2 + \left( \frac{(4/3) \omega^2 \tau_v^2}{1 + \omega^2 \tau_v^2} \right) \quad \ldots \ldots (19)$$

where $\tau_v$ and $\tau_o$ are the bulk and shear relaxation times, which are equal to $\eta_v/K_2$ and $\eta_o/G_2$, respectively. According to the theory of viscoelasticity, the complex longitudinal modulus $M^*$ is

$$M^* = K^* = \frac{4}{3} G^* = \frac{K_o}{1 + \omega^2 \tau_v^2} + \frac{(4/3) G_o}{1 + \omega^2 \tau_v^2}$$

In the following sections, the dispersions of acoustic properties are interpreted using the relaxation model, Eq. (20), given by Herzfeld and Litovitz.\(^{(19)}\)

### 4.2. Frequency Dependency of Sound Velocity $c$

It can be seen from Figs. 6 and 7 that the sound velocity increases as increasing frequency at an identical temperature in the dispersion (unrelaxed) region. Combination of Eq. (20) and Eq. (A16) gives the real part of complex longitudinal modulus $M^*$ as follows:

$$M^* = \frac{\alpha \omega \rho c^2}{\pi} = \frac{K_o}{1 + \omega^2 \tau_v^2} + \frac{(4/3) G_o}{1 + \omega^2 \tau_v^2} \quad \ldots \ldots (22)$$

According to the absolute reaction rate theory by Eyring,\(^{(22)}\) the shear viscosity can be expressed by Arhrenius expression using the activation energy for shear viscosity $E_c$:

$$\eta_c = \eta_0 \exp\left( \frac{E_c}{RT} \right) \quad \ldots \ldots (23)$$

where $R$ is the gas constant, $T$ is the absolute temperature and $\eta_0$ is the pre-exponential factor. Assuming that the bulk viscosity is also due to the activation process,

$$\eta_v = \eta_0 \exp\left( \frac{E_v}{RT} \right) \quad \ldots \ldots (24)$$

where $E_v$ is the activation energy for bulk viscosity and $\eta_0$ is the pre-exponential factor. Substituting Eqs. (23) and (24) into Eq. (22) leads to

$$M^* = \frac{\alpha \omega \rho c^2}{\pi} \quad \ldots \ldots (25)$$

$\tau_v = \eta_0/K_2$. Therefore, in order to calculate the $M^*$ values by Eq. (25), six unknowns $\eta_0, E_v, G_v, K_v, \tau_v$, and $E_v$ should be fixed. The $\eta_0$ and $E_v$ values have been derived by the least square fitting of the viscosity data\(^{(22)}\) as follows:

\begin{table}[h]
\centering
\caption{The $\eta_0$, $E_v$, $G_v$, $K_v$, $\tau_v$, and $E_v$ values used in this study.}
\begin{tabular}{lcccccc}
\hline
& $\eta_0$ & $E_v$ & $G_v$ & $K_v$ & $\tau_v$ & $E_v$ \\
\hline
33Na$_2$O-67SiO$_2$ & 1.4 & 170 & 7.0 & 9.0 & 1.5 & 100 \\
33K$_2$O-67SiO$_2$ & 0.61 & 190 & 4.0 & 6.0 & 0.9 & 120 \\
\hline
\end{tabular}
\end{table}

\(<2012 ISIJ International, Vol. 52 (2012), No. 10>\)
ues to the $\alpha \Delta c^2/\pi$ versus $T$ curves assuming that six parameters are temperature-independent. It has been reported that $G_\infty$ for silicate melts is essentially composition- and temperature-insensitive, and is taken to be 3–31 GPa. $G_\infty$ in this study is in the range of reported values. However, there is no report with respect to the $K_\infty$, $\tau_0$ and $E_v$ values. As for the $M^\infty$ versus $T$ curves in Fig. 10, the $G_\infty$ and $K_\infty$ values affect the peak height, while the $E_v$ and $\tau_0$ values determine the full width at half maximum and the peak position, respectively. It is confirmed by varying the substituted $G_\infty$, $K_\infty$, $\tau_0$ and $E_v$ values that $E_v$ is the most sensitive parameter for fitting; ±20% change in $E_v$ causes the calculated $M^\infty$ values to dramatically deviate from the $\alpha \Delta c^2/\pi$ values. As a consequence, the $E_v$ value is considered to be a reliable parameter.

4.4. Bulk Relaxation Process Estimated by Activation Energy of Bulk Viscosity

Bulk and shear relaxations, which are associated with bulk and shear viscosities, can be illustrated in the similar fashion to Fig. 8 although Fig. 8 originally exhibits the elastic deformation instead of plastic one. Bulk relaxation yields the volumetric change, and shear relaxation does not. Table 1 shows that the activation energies for bulk viscosity are 100 and 120 kJmol$^{-1}$ for $\gamma$-$\text{Na}_2\text{O} \cdot \text{SiO}_2$ and $\gamma$-$\text{K}_2\text{O} \cdot \text{SiO}_2$, respectively, which are both 70 kJmol$^{-1}$ less than those for shear viscosity.

Oishi et al. have measured the self-diffusion coefficients of oxygen for some silicate melts by a gas-liquid exchange technique using $^{18}$O as tracer, and have found that the activation energies of self-diffusion of oxygen are close to their respective activation energies of shear viscous flow. They have proposed that the shear viscous flow may be rate-controlled by the diffusion of oxygen ions in silicate melts by the closeness of two activation energies. Webb have also reported that the structural relaxation responsible for the shear viscosity is the making and breaking of Si–O bonds in the melts, i.e., oxygen exchange between bridging and non-bridging sites.

On the other hand, as shown in Fig. 8, the bulk relaxation is associated with the volumetric change in volume element. Forry have measured the internal friction of the $\text{Na}_2\text{O} \cdot \text{SiO}_2$ glasses, and have revealed that the internal friction versus temperature curves have two distinct peaks having the activation energies of 66 and 120 kJmol$^{-1}$ for $\gamma$-$\text{Na}_2\text{O} \cdot \text{SiO}_2$. He has suggested that the relaxation with the higher activation energies arises from cooperative action of two activated sodium ions. Since the activation energy due to the cooperative action of two Na$^+$ ions is close to the activation energy of bulk viscosity in Table 1, it may be considered that the bulk relaxation stems from the cooperative action of two cations. Namely, the cooperative movement of two cations, which binds two O$^-$ ions in the $\equiv\text{Si} \cdot \text{O} \cdot \text{Si} \equiv$ bond, may change the relative position of two O$^-$ ions and/or bond angle, resulting in the bulk relaxation.

5. Conclusions

The temperature and the frequency dependencies of velocities and absorption coefficients of ultrasonic waves have been measured on molten alkali silicates ($33(\text{mol}%)\text{M}_2\text{O} \cdot \text{SiO}_2$ (M = Na and K)) using the pulse transmission technique, so as to elucidate the relaxation phenomena of ultrasonic waves. The velocities and the absorption coefficients have been determined by the Fourier transform of ultrasonic pulses. It has been found that the ultrasonic velocities, $c$, increases with decreasing temperature, while the absorption per wavelength, $\alpha \lambda$, increases and then decreases with decreasing temperature. It has also been found that the $c$ and $\alpha \lambda$ values are identical irrespective of frequencies above ca. 1.400 K for $\gamma$-$\text{Na}_2\text{O} \cdot \text{SiO}_2$ and ca. 1.500 K for $\gamma$-$\text{K}_2\text{O} \cdot \text{SiO}_2$, respectively, while dispersion, i.e., frequency dependency, appears below these temperatures as follows: (1) the sound velocity increases as increasing frequency at constant temperature in the dispersion (unrelaxed) region, and (2) the peak temperature of the $\alpha \lambda$ versus $T$ curve, corresponding to the glass transition temperature, increases with increasing frequency. The dispersions of acoustic properties have been successfully interpreted using the relaxation model given by Herzfeld and Litovitz. The activation energies of bulk viscosity, which are determined by the model, are found to be 100 and 120 kJmol$^{-1}$ for $\gamma$-$\text{Na}_2\text{O} \cdot \text{SiO}_2$ and $\gamma$-$\text{K}_2\text{O} \cdot \text{SiO}_2$, respectively. Since the activation energy due to the cooperative action of two Na$^+$ ions is close to the activation energy of bulk viscosity for $\gamma$-$\text{Na}_2\text{O} \cdot \text{SiO}_2$, it may be considered that the bulk relaxation stems from the cooperative action of two cations. Namely, the cooperative movement of two cations, which binds two O$^-$ ions in the $\equiv\text{Si} \cdot \text{O} \cdot \text{Si} \equiv$ bond, may change the relative position of two O$^-$ ions and/or bond angle, resulting in the bulk relaxation.

Nomenclature

- $a$: spacing between atoms
- $b(x, \omega)$: amplitude of the Fourier transform of a ultrasonic pulse
- $c$: velocity of ultrasonic waves
- $c^*$: complex velocity of ultrasonic waves
- $c_0$: velocity of ultrasonic waves for $\omega^2\tau << 1$
- $C$: spring constant between atoms
- $E_v$: activation energy for shear viscosity
- $F_v$: activation energy for bulk viscosity
- $f$: frequency of ultrasonic waves
- $G$: shear modulus
- $G^*$: complex shear modulus
- $G_\infty$: high-frequency shear modulus
- $K$: bulk modulus
- $K^*$: complex bulk modulus
- $K_0$: zero frequency bulk modulus
- $K_v$: relaxation part of bulk modulus, $K_v = K_\infty - K_0$
- $K_\infty$: high-frequency bulk modulus
- $M$: longitudinal (elastic) modulus
- $M^*$: complex longitudinal modulus
- $M_\infty$: real part of complex longitudinal modulus
- $M^\infty$: imaginary part of complex longitudinal modulus
- $R$: gas constant
- $T$: absolute temperature
- $k$: wave vector
- $k^*$: complex wave vector
- $p$: acoustic pressure
- $s = -\partial u/\partial x$, meaning the relative density change or condensation
\( w \): displacement of atoms (or amplitude of a pulse)  
\( \alpha \): absorption coefficient of ultrasonic waves  
\( \beta_s \): adiabatic compressibility  
\( \eta \): longitudinal viscosity  
\( \eta_s \): shear viscosity  
\( \delta \): bulk viscosity  
\( \lambda \): wavelength of ultrasonic waves  
\( \rho \): density of the sample  
\( \tau \): viscous relaxation time  
\( \tau_s \): shear relaxation time  
\( \phi(x, \omega) \): phase of the Fourier transform of a ultrasonic pulse  
\( \omega \): angular frequency of ultrasonic waves  
\( \Delta \): distance between two ends of the buffer rods  
\( \Delta t \): time required for the transmission of the ultrasonic pulses

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\[ F_i = C(u_{i+1} - u_i) + C(u_{i-1} - u_i) \]  ............... (A1)

From the equation of motion,
\[ m \frac{d^2 u_i}{dt^2} = F_i = C(u_{i+1} + u_{i-1} - 2u_i) \]  ............... (A2)

where \( m \) is the mass of an atom. The displacement of atoms \( u \) can be expressed by Eq. (8) and \( x = sa \) (\( a \) is the spacing between atoms) is substituted into Eq. (8). Then,
\[ u_s = u_0 \exp \{i(\omega t - ska)\} \]  ............... (A3)

Substituting Eq. (A3) into Eq. (A2) yields
\[ -\omega^2 u_0 \exp \{i(\omega t - ska)\} = Cu_0 \exp \{i(\omega t - (s + 1)ka)\} \]  
\[ + \exp \{i(\omega t - (s - 1)ka)\} - \exp \{i(\omega t - ska)\} \]  ............... (A4)

Division by \( u_0 \exp \{i(\omega t - ska)\} \) and adopting the equality
\[ 2\cos(ka) = \exp(ika) + \exp(-ika) \]  gives
\[ \omega^2 = \frac{2C}{m} (1 - \cos ka) = \frac{4C}{m} \sin^2 \frac{1}{2} ka \]  ............... (A5)

Since \( c = \omega / k \), then,
\[ c = a \frac{C}{\sqrt{\rho}} \]  ............... (A7)

By substituting \( \rho = ma^2 \) and \( F = Cu \) (Hooke’s law) into the stress-strain relation, i.e., \( F/a^2 = Mu/a \), we can obtain \( C = Ma \). Then,
\[ c = a \frac{M}{\sqrt{\rho}} \]  ............... (A8)

\( M = K + \frac{4}{3} G \) owing to the theory of viscoelasticity. When the shear modulus \( G \) is negligibly small,
\[ \beta = \frac{1}{K} = \frac{1}{\rho c^2} \]  ............... (A9)

Equation (A2) can also be described by the following,
\[ m \frac{d^2 u}{a^2 dt^2} = C \frac{u_{i+1} - u_i - u_i - u_{i-1}}{a} \]  ............... (A10)

Since the relation \( u/a = \partial u/\partial x \) is hold, then,
\[ \frac{\partial^2 u}{\partial t^2} = M \frac{\partial^2 u}{\partial x^2} \]  ............... (A11)

Substitution of Eq. (8) into Eq. (A11) also gives Eq. (A8).

The effects of absorption can be incorporated by using a complex wave number \( k' = k - \alpha i \) (see Eq. (9)), a complex longitudinal elastic modulus \( M' \) and a complex velocity of ultrasonic waves \( c^* \). Eq. (A8) is rewritten as
\[ c^* = \frac{M'}{\rho} = \frac{M' + iM''}{\rho} \]  ............... (A11)

The displacement \( u \) of the wave is
\[ u = w_0 \exp\{i(\omega t - k^*x)\} = w_0 \exp\{i\omega(t - (k^*/\omega)x)\} \]

Consequently,

\[ \frac{1}{c'} = \frac{k^* - i\alpha}{\omega} = \frac{\omega}{c} - i\frac{\alpha}{\omega} = \frac{1}{c} - i\frac{\alpha}{\omega} \] ........................ (A13)

From Eqs. (A11) and (A13), we can obtain

\[ M' = \rho c^2 \left\{ \frac{1}{1 + \left(\frac{\alpha c}{\omega}\right)^2} \right\} \] ........................ (A14)

\[ M'' = \rho c^2 \left\{ \frac{2}{1 + \left(\frac{\alpha c}{\omega}\right)^2} \right\} \] ........................ (A15)

When \( \alpha c/\omega = \alpha \lambda/2\pi <<1 \), Eqs. (A14) and (A15) are approximated into these equations,

\[ c = \sqrt{\frac{M'}{\rho}} \] .............................. (A16)

\[ \alpha = \frac{\omega M''}{2\rho c^3} \] ............................... (A17)

**Appendix II. Fourier Transform of an Ultrasonic Pulse to Obtain the Frequency Dependency of Acoustic Properties**

According to the Fourier integral theorem, arbitrary function \( f(t) \) can be described as following.

\[ f(t) = \frac{1}{\pi} \int_0^\infty \{ A(\omega) \cos \omega t + B(\omega) \sin \omega t \} d\omega \]

\[ A(\omega) = \int_{-\infty}^\infty f(t) \cos \omega t dt \] ........................ (A18)

\[ B(\omega) = \int_{-\infty}^\infty f(t) \sin \omega t dt \]

where \( A(\omega) \) and \( B(\omega) \) are the Fourier cosine and sine transform, respectively. Eq. (A18) can be converted into Eq. (A19)

\[ f(t) = \frac{1}{\pi} \int_0^\infty a(\omega) \cos (\omega t - \phi) d\omega \] ........................ (A19)

When an ultrasonic pulse travels at the velocity of \( c \) in the positive \( x \) direction, the time function of the pulse at \( x \) can be described as

\[ f(x,t) = \frac{1}{\pi} \int_0^\infty e^{-i\alpha(\omega)} a(\omega) \cos \left\{ \omega \left( t - \frac{x}{c(\omega)} \right) - \phi \right\} d\omega \] ........................ (A20)

From the Fourier transform of Eq. (A20), we can obtain the following amplitude \( b(x, \omega) \) and phase \( \phi(x, \omega) \).

\[ b(x, \omega) = \frac{1}{\pi} e^{-i\alpha(\omega)} a(\omega) \] ........................ (A21)

\[ \phi(x, \omega) = \omega \left( \frac{x}{c(\omega)} \right) + \phi \] ........................ (A22)

In an analogous way, the amplitude and phase of the Fourier transform of the time function at \( x + \Delta x \) are

\[ b(x + \Delta x, \omega) = \frac{1}{\pi} e^{-i\alpha(\omega)(x + \Delta x)} a(\omega) \]

\[ = e^{-i\alpha(\omega)\Delta x} b(x, \omega) \] ........................ (A23)

\[ \phi(x + \Delta x, \omega) = \omega \left( \frac{x + \Delta x}{c(\omega)} \right) + \phi \]

\[ = \omega \left( -\Delta t + \frac{x + \Delta x}{c(\omega)} \right) + \phi(x, \omega) \] ........................ (A24)

where \( \Delta t \) is the delay time of a received pulse when transmission distance of the pulse is extended from \( x \) to \( x + \Delta x \).

From Eq. (A23),

\[ -\alpha(\omega)\Delta t = \ln \left( \frac{b(x + \Delta x, \omega)}{b(x, \omega)} \right) \] ........................ (A25)

As a result, the slope of the \( \ln\{b(x + \Delta x, \omega)/b(x, \omega)\} \) versus \( \Delta x \) curve gives \(-\alpha(\omega)\). On the other hand, from Eq. (A24),

\[ \omega\Delta t + \phi(x + \Delta x, \omega) - \phi(x, \omega) = \omega\Delta x/c(\omega) \] ........................ (A26)

Equation (A26) indicates that the slope of the \( \omega\Delta t + \phi(x + \Delta x, \omega) - \phi(x, \omega) \) versus \( \Delta x \) curve gives \( c(\omega) \). 

**Figures 11 and 12** show a typical \( \ln\{b(x + \Delta x, \omega)/b(x, \omega)\} \) versus \( \Delta x \) curve and a \( \omega\Delta t + \phi(x + \Delta x, \omega) - \phi(x, \omega) \) versus \( \Delta x \) curve, respectively.
Appendix III. Maxwell Model for Absorption of Ultrasonic Waves

The Maxwell model shown in Fig. 1(b) assumes that the acoustic pressure \( p \) and \( s = -\partial u / \partial x \) (\( u \) is the displacement of atoms) of the elastic \( (p_1 \) and \( s_1) \) and viscous \( (p_2 \) and \( s_2) \) terms have the following relation:

\[
\begin{align*}
  s &= s_1 + s_2  \quad \text{.......................... (A27)} \\
  p &= p_1 = p_2  \quad \text{.......................... (A28)}
\end{align*}
\]

From the Hooke’s law and Newton’s law of viscosity,

\[
\begin{align*}
  p_1 &= M s_1  \quad \text{.......................... (A29)} \\
  p_2 &= \eta \frac{\partial s}{\partial t}  \quad \text{.......................... (A30)}
\end{align*}
\]

where \( M \) is the longitudinal modulus and \( \eta \) is the longitudinal viscosity. From Eqs. (A27) through (A30),

\[
\frac{\partial s}{\partial t} = \frac{1}{M} \frac{\partial p}{\partial t} + \frac{p}{\eta}  \quad \text{.................. (A31)}
\]

Since \( p = M^* s \) (\( M^* \) is the complex longitudinal modulus),

\[
\frac{\partial s}{\partial t} = \frac{M^*}{M} \frac{\partial s}{\partial t} + \frac{M^*}{\eta} \epsilon  \quad \text{.................. (A32)}
\]

By using a viscous relaxation time \( \tau = \eta/M \), Eq. (A32) can be rewritten by Eq. (A33).

\[
\frac{\partial s}{\partial t} = -\frac{M^*}{\tau (M^* - \eta)} s  \quad \text{.................. (A33)}
\]

By substituting the relation \( s = -\partial u / \partial x = s_0 \exp(i \omega t) \) into Eq. (A33),

\[
M^* = M \left( \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} + i \frac{\omega \tau}{1 + \omega^2 \tau^2} \right)  \quad \text{.................. (A34)}
\]