

RELATION BETWEEN ACOUSTIC PROPERTIES AND STRUCTURES ON MOLTEN ALKALI SILICATES

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Abstract

Temperature and frequency dependencies of velocities and absorption coefficients of ultrasonic waves were measured on molten 33(mol%)Na₂O-SiO₂ and 33(mol%)K₂O-SiO₂, and compositional dependencies of ultrasonic velocities were summarized using previous data on molten M₂O-SiO₂ (M = Li, Na and K) so as to elucidate the relation between acoustic properties and silicate network structures. The velocities and absorption coefficients of ultrasonic waves are identical irrespective of frequencies above ca. 1400 K for 33Na₂O-67SiO₂ and ca. 1500 K for 33K₂O-67SiO₂, respectively, while frequency dependencies appear below these temperatures. Frequency dependency stems from the structural relaxation of molten silicates. It has also been found that there is an identical linear relation between the ultrasonic velocities and the molar volumes for these alkali silicates. This indicates that the molar volume is one of the most significant factors affecting the ultrasonic velocity value instead of the ionicity of atomic bonding.

Introduction

Ultrasonic waves could be useful for refining processes. For example, size and distribution of nonmetallic inclusions in molten steel and thickness of refractory walls of blast furnace can be estimated 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. Ultrasonic waves propagate in materials as lattice vibration in analogy with thermal conduction. Mills has proposed that the thermal conductivities of molten silicates at their liquidus temperatures linearly decrease with increasing the ratio of the number of non-bridging oxygen atoms to that of tetrahedrally-coordinated atoms such as Si (denoted as NBO/T)¹. Nagata et al.² have reported that the ultrasonic velocities in the Na₂O-SiO₂ and PbO-SiO₂ systems at 1400 K decrease with decreasing silica contents, i.e., increasing NBO/T. As a consequence, it might be possible that ultrasonic velocities have the similar structural dependencies to thermal conductivities. However, the compositional dependency of ultrasonic velocities on molten silicates has not been intensively discussed from the viewpoint of the structures. One of the reasons that the compositional dependency has not been elucidated yet is that there are large discrepancies among reported ultrasonic velocities of molten silicates. Therefore, in this paper, previous data of ultrasonic velocities on molten silicates were reviewed at first, and then the compositional dependency of ultrasonic velocities of molten alkali silicates were discussed from structural viewpoint. As for the temperature dependency of acoustic properties, the ultrasonic velocity of molten silicates generally decreases with increasing

temperature. Although molten silicates exhibit so-called glass transition, there are very few reports with respect to the temperature dependency of acoustic properties of silicates around glass transition temperatures. Another aim of this paper is to measure the temperature dependencies of velocities and absorption coefficients of ultrasonic waves on molten alkali silicates so as to discuss the variation of acoustic properties with temperature around the glass transition temperature.

Experimental

The temperature and the frequency dependencies of velocities and absorption coefficients of ultrasonic waves have been measured on molten alkali silicates using the pulse transmission technique. Master glasses of (mol%) $33\text{M}_2\text{O}\cdot 67\text{SiO}_2$ ($\text{M} = \text{Na}$ and K) were prepared from reagent grade SiO_2 , Na_2CO_3 and K_2CO_3 powders. Powders were dried enough at elevated temperatures. Weighed mixtures of SiO_2 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 by pouring the melts onto a copper plate and crushed to obtain the samples. Figure 1 shows the schematic diagram of 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 rods (30 mm in diameter and 265 mm in length) made of high-density polycrystalline alumina. The piezoelectric transducers of BaTiO_3 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.

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).

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 remove air bubbles contained in the sample. After degassing, the vacuum pump 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. At each measurement temperature, 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 $10\ \mu\text{m}$. The transmission times were acquired for nine to ten different distances between two ends of the rods.

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 continuous frequencies instead of a single wave. Therefore, the values of c and α have been determined using Fourier transform. The detail of the analysis was described in elsewhere.³⁾

Temperature Dependencies of Acoustic Properties³⁾

Figures 2 and 3 show the temperature dependencies of the c and $\alpha\lambda$ values at 1.2, 3.6 and 6.0 MHz for $33\text{Na}_2\text{O}\cdot 67\text{SiO}_2$ and $33\text{K}_2\text{O}\cdot 67\text{SiO}_2$, respectively, where λ is the wavelength of ultrasonic waves. $\alpha\lambda$ means the absorption per wavelength. Figs. 2 and 3 also include previous data.^{4,5)} 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 α values measured by changing the position of the upper buffer rod nine to ten times. The measurements for $33\text{Na}_2\text{O}\cdot 67\text{SiO}_2$ and $33\text{K}_2\text{O}\cdot 67\text{SiO}_2$ were carried out until 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. It can be seen from Figs. 2 and 3 that the c and $\alpha\lambda$ values are identical irrespective of frequencies above ca. 1400 K for $33\text{Na}_2\text{O}\cdot 67\text{SiO}_2$ and ca. 1500 K for $33\text{K}_2\text{O}\cdot 67\text{SiO}_2$, respectively, while frequency dependency appears below these temperatures. Frequency dependency stems from the structural relaxation of molten silicates, which can be explained as follows: Molten silicates exhibit "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 equilibrium, 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. It has been reported that the conventional "glass transition temperatures" obtained by thermal expansion measurement are 729 K for $33\text{Na}_2\text{O}\cdot 67\text{SiO}_2$ and 755 K for $33\text{K}_2\text{O}\cdot 67\text{SiO}_2$.⁶⁾ In ultrasonic studies, the observation timescale is microseconds instead of seconds for thermal expansion. Hence, the temperature around which the relaxation occurs is raised by several hundred degrees above the conventional glass transition temperatures.

It is found from Figs. 2 and 3 that the $\alpha\lambda$ value increases and then decreases with decreasing temperature. This can be explained as follows: For a liquid at high temperatures, the structure is in equilibrium and the response of a melt to acoustic pressure is instantaneous. Upon cooling of the liquid into the glass transition region, the response of a melt to acoustic pressure is delayed. The absorption of acoustic energy is associated with this delay between acoustic pressure and the medium response (density or volume change). As decreasing temperature, the delay becomes larger, and the absorption of acoustic energy becomes greater. However, when the temperature decreases further, the structure of the glass is becoming frozen and hardly responds to acoustic pressure, resulting in the less absorption of acoustic energy. Consequently, the peak temperature of the $\alpha\lambda$ versus T curve corresponds to the glass transition temperature for ultrasonic waves.

Figure 4 shows the reciprocal of glass transition temperature versus logarithm of the reciprocal of frequency, that is, logarithm of the observation time. Here, it is assumed that the observation time is 1 s for thermal expansion. It can be seen that there is an identical relation between glass transition temperatures and observation times for the different observation techniques of glass transition temperatures, as Webb has suggested.⁷⁾

Compositional Dependencies of Ultrasonic Velocities⁸⁾

Figures 5 through 7 show the reported ultrasonic velocities of the M_2O - SiO_2 systems ($M = Li, Na$ and K) at 1573 K as a function of the M_2O content. The velocity of the Li_2O - SiO_2 system increases from ca. $2700 \text{ m} \cdot \text{s}^{-1}$ to ca. $3200 \text{ m} \cdot \text{s}^{-1}$ with increasing the Li_2O content from 30 mol% to 60 mol% except for the data reported by Bloom and Bockris.⁹⁾ With respect to the discrepancy between the data by Bloom and Bockris and others, Baidov and Kunin¹⁰⁾ and Rivers and Carmichael¹¹⁾ have pointed out that the alumina buffer rods that Bloom and Bockris used may have been seriously corroded in the melts during the experiment. Corrosion of alumina buffer rods would increase the true wave path length in the melts, leading to an underestimate of the sound speed. The velocity of the Na_2O - SiO_2 system slightly increases from ca. $2500 \text{ m} \cdot \text{s}^{-1}$ to ca. $2700 \text{ m} \cdot \text{s}^{-1}$ with increasing the Na_2O content from 15 mol% to 60 mol% except for the data reported by Shiraishi et al.¹²⁾ The reason for the deviation in the results of Shiraishi et al. is not clear. On the other hand, the velocity of the K_2O - SiO_2 system decreases from ca. $2400 \text{ m} \cdot \text{s}^{-1}$ to ca. $1800 \text{ m} \cdot \text{s}^{-1}$ with an increase in the K_2O content from 20 mol% to 50 mol% except for the value obtained by Shiraishi et al.,¹²⁾ which is much higher than other data. They have used an ultrasonic frequency as large as 10 MHz while other researchers have used frequencies less than 4 MHz. As aforementioned, the ultrasonic velocity is generally independent of the frequency of waves, i.e., dispersionless. Dispersion means that the velocity varies with frequency. In fact, dispersion happens at very high frequencies (for example, with thermal phonons near the Brillouin zone boundaries) or for high viscous materials, in which part of the atomic movements cannot follow high frequencies of ultrasonics. In such an unrelaxed region, the velocity increases with an increase in the frequency. In fact, Bidov and Kunin¹⁰⁾ have measured the velocities at the frequencies of 1 and 4.7 MHz, and have observed the dispersion in the melts of K_2O - SiO_2 having viscosities of the order of magnitude $100 \text{ Pa} \cdot \text{s}$. Therefore, it is considered that 10 MHz is the frequency far above the relaxation region of the melt, and Shiraishi et al. have measured an unrelaxed ultrasonic velocity.

It is surprising that the ultrasonic velocities do not always decrease with decreasing silica contents, i.e., increasing NBO/T. Figure 8 shows the relation between the ultrasonic velocities at 1573 K and the molar volumes.⁸⁾ It can be found that there is an identical linear relation between the ultrasonic velocities and the molar volumes. This indicates that the molar volume is one of the most significant factors affecting the ultrasonic velocity value. The difference between thermal conductivity and ultrasonic velocity with respect to their dependencies on NBO/T can be explained as follows: Vibrational cycles of thermal phonons (GHz to THz) are shorter than the average times required for the cutting and bridging of Si-O-Si bonds due to the movement of metallic ions. As a result, conductive heat transfer occurs reflecting the ionicity (or covalency) of atomic bonding. On the other hand, vibrational cycles of acoustic waves are longer than the times for the rearrangement of silicate structures. Therefore, the transfers of acoustic waves may be hardly affected by the ionicity of atomic bonding.

Conclusions

Temperature and frequency dependencies of velocities and absorption coefficients of ultrasonic waves were measured on molten $33(\text{mol}\%)Na_2O$ - SiO_2 and $33(\text{mol}\%)K_2O$ - SiO_2 , and compositional dependencies of ultrasonic velocities were summarized on molten M_2O - SiO_2 ($M =$

Li, Na and K) so as to elucidate the relation between acoustic properties and silicate network structures. The following results were obtained:

- (1) The velocities and absorption coefficients of ultrasonic waves are identical irrespective of frequencies above ca. 1400 K for $33\text{Na}_2\text{O}\cdot 67\text{SiO}_2$ and ca. 1500 K for $33\text{K}_2\text{O}\cdot 67\text{SiO}_2$, respectively, while frequency dependency appears below these temperatures. Frequency dependency stems from the structural relaxation of molten silicates.
- (2) There is an identical linear relation between the ultrasonic velocities and the molar volumes for various alkali silicates. This indicates that the molar volume is one of the most significant factors affecting the ultrasonic velocity value.

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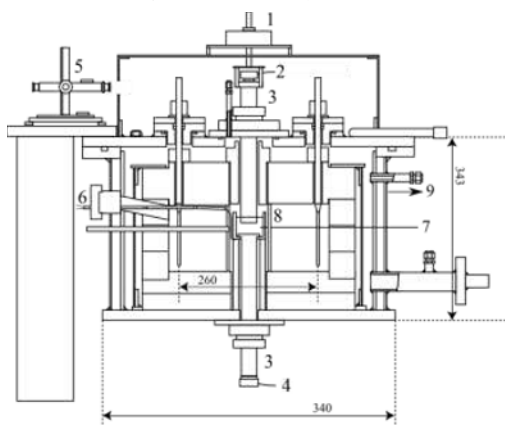


Fig.1 Schematic diagram of the experimental apparatus with actual dimensions (mm). 1. Induction motor, 2. Receiver, 3. Al_2O_3 rod, 4. Pulsar, 5. Cathetometer, 6. Thermocouple, 7. Sample, 8. Ceramics tube, 9. Vacuum pump.

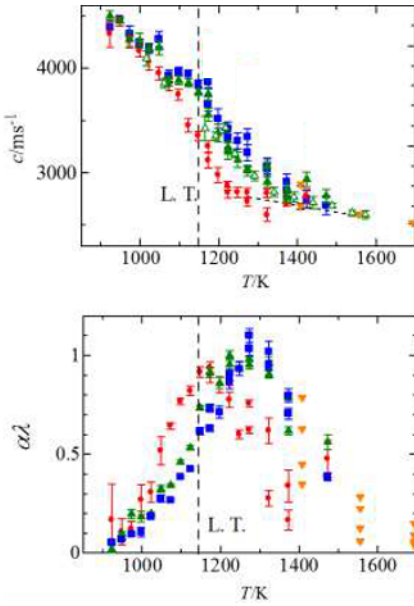


Fig.2 Temperature dependencies of the c and $\alpha\lambda$ values at various frequencies (\circ 1.2 MHz, \triangle 3.6MHz and \square 6.0MHz) for $33\text{Na}_2\text{O}\cdot 67\text{SiO}_2$. The dashed line after Bockris and Kojonen.⁴⁾

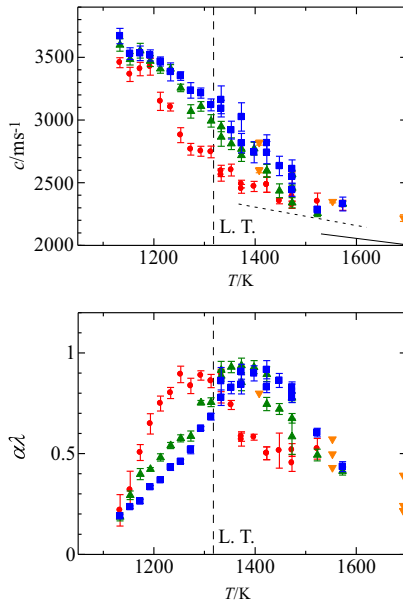


Fig.3 Temperature dependencies of the c and $\alpha\lambda$ values at various frequencies (\circ 1.2 MHz, \triangle 3.6MHz and \square 6.0MHz) for $33\text{K}_2\text{O}\cdot 67\text{SiO}_2$. The plain line after Baidov and Kunin⁵⁾ and the dashed line after Bockris and Kojonen⁴⁾.

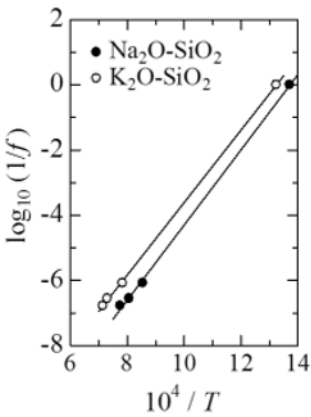


Fig.4 Reciprocal of glass transition temperature versus logarithm of the reciprocal of frequency, that is, logarithm of the observation time.

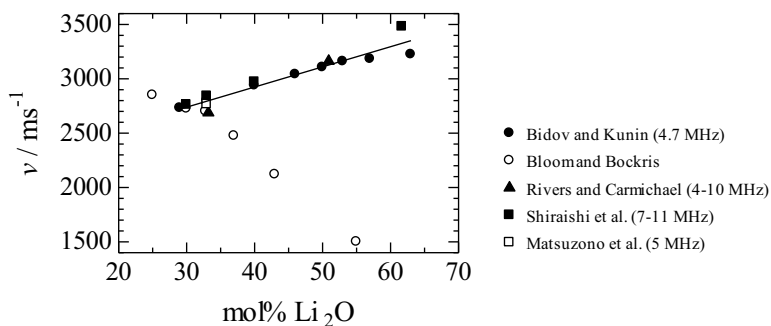


Fig.5 Velocities of the $\text{Li}_2\text{O-SiO}_2$ systems at 1573 K as a function of the Li_2O content (mol%).

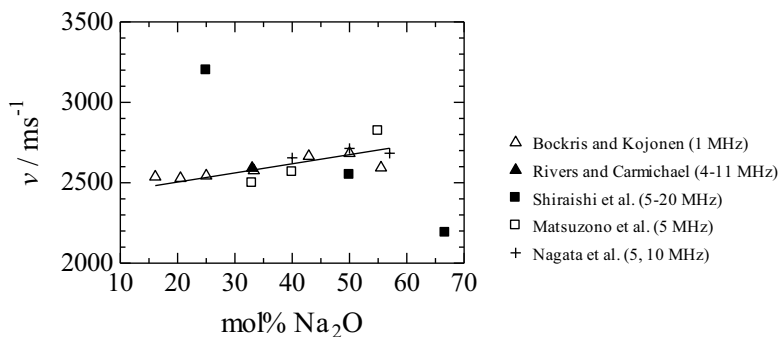


Fig.6 Velocities of the $\text{Na}_2\text{O-SiO}_2$ systems at 1573 K as a function of the Na_2O content (mol%).

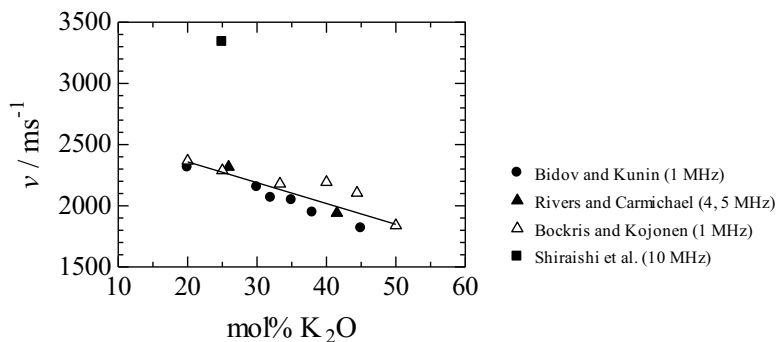


Fig.7 Velocities of the $\text{K}_2\text{O-SiO}_2$ systems at 1573 K as a function of the K_2O content (mol%).

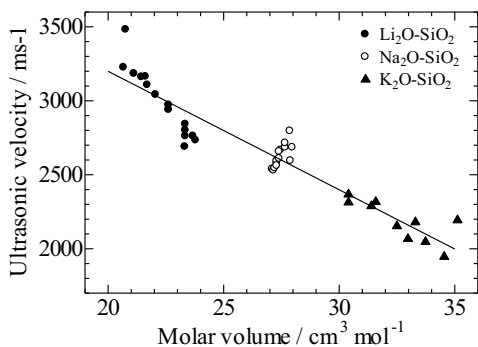


Fig.8 Velocities of the M₂O-SiO₂ systems (M = Li, Na and K) at 1573 K as a function of the M₂O content (mol%).