

Ultrasonic properties of silica aerogels at low temperatures

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We have made ultrasonic measurements on several silica aerogels in the previously unstudied region between room temperature and 15 K. We present detailed results for two samples with densities of 360 and 290 kg/m³ (porosities of 84 and 89%) and sound velocities of a few hundred meters per second. Below about 120 K, both longitudinal and transverse sound velocities increased substantially (by up to 16%, much more than in bulk glasses). These velocity changes were almost frequency independent and were accompanied by attenuation peaks whose magnitude increased linearly with frequency. The maximum attenuation was so large, nearly 400 dB/cm at 10 MHz in the lower-density sample, that measurements could only be made below about 15 MHz. Below about 40 K, the attenuation was proportional to the cube of the temperature. The velocity changes and attenuation peaks resemble, but are much larger than, those seen in bulk dielectric glasses where they are associated with a relaxation process but the origin of the T^3 attenuation is unclear. [S0163-1829(98)02605-8]

INTRODUCTION

Silica aerogels are porous glasses made via a sol-gel process and subsequent hypercritical drying. This process produces tenuous solid structures with densities ρ as small as 5 kg/m³ (corresponding to a porosity $\phi=99.8\%$) and unique acoustic and thermal properties. Ultrasonic measurements,¹ for example, find very low sound speeds, as low as 20 m/s in the highest porosity materials. Thermal measurements at low temperatures indicate substantial differences between excitations in aerogels and bulk glasses. In bulk glasses,² the behavior of both the heat capacity and the thermal conductivity below 1 K is dominated by the “two level systems” (TLS’s) that characterize amorphous materials. These TLS’s result in a heat capacity which is larger than the Debye prediction and varies linearly with temperature as well as a thermal conductivity which varies as T^2 . At higher temperatures, a characteristic heat capacity “bump” and a thermal conductivity plateau are observed. In silica aerogels³⁻⁵ a heat capacity that varies nearly linearly with temperature is also found below 2 K. However, in contrast to bulk glasses, this heat capacity is smaller than the very large Debye T^3 heat capacity that the low sound speeds would predict (although still several orders of magnitude larger than that of bulk silica). The thermal conductivity in aerogels is much smaller than in bulk glasses and shows neither the low-temperature T^2 dependence nor a plateau at higher temperatures. Instead, there appears to be a plateau below 1 K and a roughly $T^{1.5}$ variation at higher temperatures.

The acoustic properties of glasses² are also very different from their crystalline counterparts. Bulk glasses have an ultrasonic attenuation peak around 70 K due to structural relaxation. Below a few kelvin, the temperature and frequency dependences of the sound velocity and attenuation are determined by interactions with TLS’s and can be used to determine their density of states. At the lowest temperatures resonant interactions dominate, causing the velocity to increase logarithmically with temperature. As the temperature increases, the relaxation of TLS’s due to thermal phonons becomes important and the velocity goes through a maximum

and then decreases. The relaxation process is also responsible for an attenuation which increases as T^3 at the lowest temperatures and then becomes nearly constant above the velocity maximum.

The open, tenuous structure of aerogels results in unique acoustic properties. Room-temperature measurements,^{1,6,7} showed that aerogels’ elastic moduli are somewhat affected by chemical composition, gel preparation conditions, and by subsequent heat treatment, but depend primarily on density. The sound speeds scale as ρ^α (where $\alpha\approx 1.35$ for aerogels denser than 100 kg/m³ and $\alpha\approx 0.8$ for lighter aerogels) and can be as low as 20 m/s (in an evacuated sample with $\rho=5$ kg/m³). The ratio of transverse and longitudinal sound speeds is about 0.60, comparable to that in bulk silica glass and corresponding to a Poisson’s ratio $\nu=0.22$. In general, base catalyzed aerogels have slightly lower sound velocities than acid catalyzed aerogels of the same density. Heating at 500 °C changes the density by only about 1%, but increases the sound velocities by 30%. Heating to higher temperatures results in substantial shrinkage, producing densified aerogels with a different microstructure and sound speeds about twice as large as untreated aerogels with the same density.

The only low-temperature acoustic measurements involving aerogels to date^{3,8} are low-frequency (kHz) sound velocity and internal friction measurements on samples with densities of 270 and 360 kg/m³ (a “densified aerogel” with $\rho=870$ kg/m³, produced by annealing, was also studied). The measurements did not extend to low enough temperature to see the characteristic logarithmic velocity increase but did show (between about 0.1 and 1 K) the velocity decrease and attenuation plateau due to TLS relaxation. However, the TLS density of states determined from these measurements was comparable to bulk glasses so TLS’s cannot account for the very large linear heat capacity. Above about 2 K the internal friction began to increase again. In the densified aerogel, where measurements extended to higher temperature, this increase was seen to be the beginning of a peak (at about 16 K) which may be related to the attenuation peak seen in bulk glasses around 70 K.

Ultrasonic (MHz) measurements on aerogels have so far

been made almost exclusively at room temperature. These showed that the attenuation in aerogels is sensitive to adsorbed water and, in low-density aerogels, to any gas within the pores. The attenuation was quite large (e.g., 30 dB/cm at 3 MHz in $\rho=129 \text{ kg/m}^3$ aerogels) and increased approximately quadratically with sound frequency. Most of the water could be removed by heating in vacuum for a few hours at 100 °C, leaving a much smaller attenuation with a weaker frequency dependence. One paper⁵ mentions that ultrasonic velocity measurements (on a 71 kg/m^3 aerogel) showed no significant variation between 300 and 30 K. Calenzuc *et al.*³ also state that the velocity of 10 MHz longitudinal and transverse waves in a densified aerogel (870 kg/m^3) varied by less than 5% from room temperature to 1.4 K.

In an attempt to determine which features of the acoustic behavior of aerogels are due to their amorphous nature and which are due to their low density and unique microstructure, we have made ultrasonic measurements in the previously unstudied region between room temperature and 15 K on a number of different silica aerogel samples. We present results for two samples with densities (360 and 290 kg/m^3) close to those used in previous acoustic measurements^{3,8} at lower temperatures. Our experiments revealed some features in common with bulk glasses, for example, attenuation peaks around 70 K, but these peaks and their associated velocity changes are much larger than in bulk glasses. In addition, we find that the attenuation below about 40 K is proportional to frequency and has a striking but unexplained T^3 temperature dependence. Preliminary results have been published elsewhere.⁹

EXPERIMENTAL DETAILS

Samples were made using a standard “one step” tetramethyl orthosilicate (TMOS) process to produce base catalyzed aerogels in the density range 360 to 42 kg/m^3 (porosities from about 84 to 98%). In this paper, we present the results of detailed measurements made on two of these, one produced in our laboratory (with a density of 290 kg/m^3), the other, denser sample (360 kg/m^3) made elsewhere.¹⁰ Thin rectangular samples (1 to 3 mm thick) were cut and LiNbO₃ transducers were attached to opposite faces using epoxy. Samples were then sealed into a copper cell, evacuated at room temperature and a small amount of helium gas was added for thermal contact. Temperatures were measured using a calibrated carbon glass sensor and controlled by a digital resistance bridge.

A phase sensitive pulse-echo technique was used to measure the velocity and attenuation of longitudinal and shear waves at several different frequencies. The large attenuation in the low-density aerogels limited the measurement frequencies to less than 15 MHz even with 1 mm thick samples. The longitudinal sound speeds at room temperature were 280 ± 30 m/s and 600 ± 30 m/s in the low- and high-density samples, respectively. The corresponding transverse sound velocities were 165 ± 20 m/s and 360 ± 20 m/s. The large uncertainties arise from the effects of the epoxy bonds, including damage to the aerogel surfaces.

RESULTS

We begin with the results from our denser ($\rho=360 \text{ kg/m}^3$) sample. Figure 1(a) compares the temperature dependence

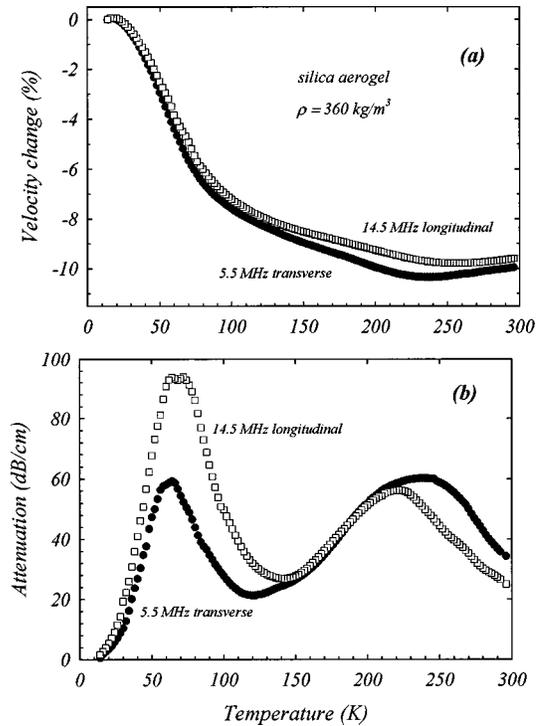


FIG. 1. (a) Temperature dependence of the ultrasonic velocity in a silica aerogel of density 360 kg/m^3 . Open squares are for longitudinal waves (14.5 MHz) and solid circles are for transverse waves (5.5 MHz). (b) Ultrasonic attenuation corresponding to the velocity data shown in (a).

dences of the sound velocity for transverse (5.5 MHz) and longitudinal (14.5 MHz) waves. Figure 1(b) shows the corresponding attenuation for the two modes. The most striking features are the attenuation peaks around 70 K. These are accompanied by velocity changes of about 8% in the region of the peaks. This behavior resembles that in bulk glasses but with much larger attenuation peaks and velocity changes. For example, the attenuation peak at 10 MHz is only about 1 dB/cm in fused silica.

Figure 2 shows the velocity changes in this sample at a number of frequencies between 3 and 16.5 MHz. The overall velocity change from low temperature to 150 K is nearly frequency independent. The maximum rates of change occur essentially at the temperatures of the attenuation peaks, which are slightly lower for the transverse modes. Figure 3 shows the damping (attenuation/frequency) corresponding to the velocities in Fig. 2. The magnitude of the peaks is independent of frequency, implying an attenuation that is proportional to frequency. The transverse modes have damping peaks that are larger by a factor of about 1.6 and these occur at slightly lower temperature (around 61 K vs 68 K for longitudinal modes). The more gradual velocity changes and broad attenuation maxima above 150 K [see in Figs. 1(a) and 1(b)] vary less systematically with frequency, although they are qualitatively the same at all frequencies. This higher temperature behavior may be associated with adsorbed water (to which the attenuation, in particular, is very sensitive⁷) or may reflect the effects of thermal expansion on the transducer bonds.

One interesting feature of Fig. 3 is the behavior of the attenuation at low temperatures. As shown in Fig. 4, below

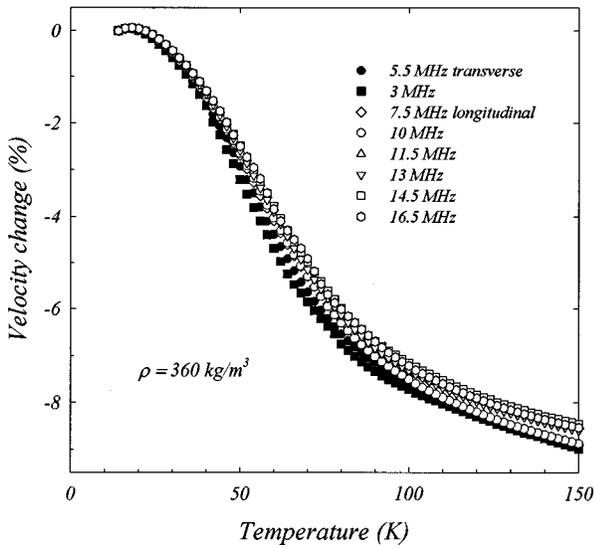


FIG. 2. Frequency dependence of the ultrasonic velocity in the sample of Fig. 1. Open symbols are for longitudinal waves (7.5 to 16.5 MHz) and solid symbols are for transverse waves (3 and 5.5 MHz).

about 30 K the damping is proportional to the cube of the temperature. This T^3 damping is independent of the frequency and is about 1.6 times larger for the transverse modes.

The general features seen in Figs. 1 to 4 are also observed in the lower density aerogels. Although the density of the second sample (290 kg/m³) is only 20% smaller than that of the first sample, its longitudinal and transverse sound speeds are substantially smaller (by factors of about 2.2). Figures 5(a) and 5(b) compare the temperature dependences of the velocity and attenuation of 10 MHz longitudinal waves in the two aerogels. The attenuation peak [Fig. 5(b)] is much larger in the lower density sample and occurs at somewhat higher temperatures. Note that the attenuation “wiggles” on the peak are experimental artifacts resulting from inadvertent interference between the ultrasonic signal and electrical

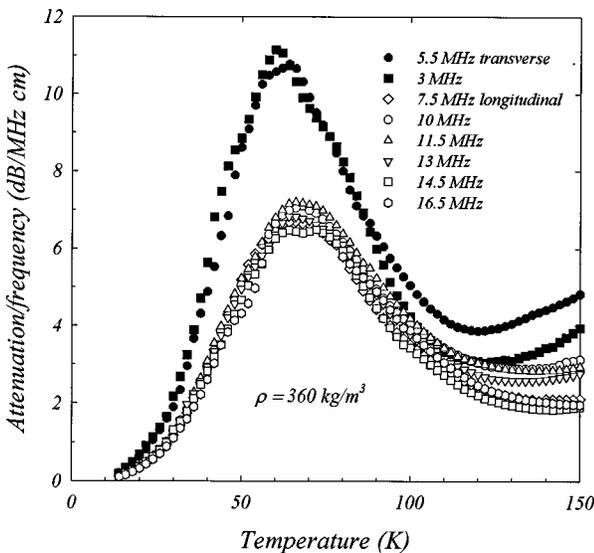


FIG. 3. Frequency dependence of the damping (attenuation/frequency) corresponding to the velocity data of Fig. 2.

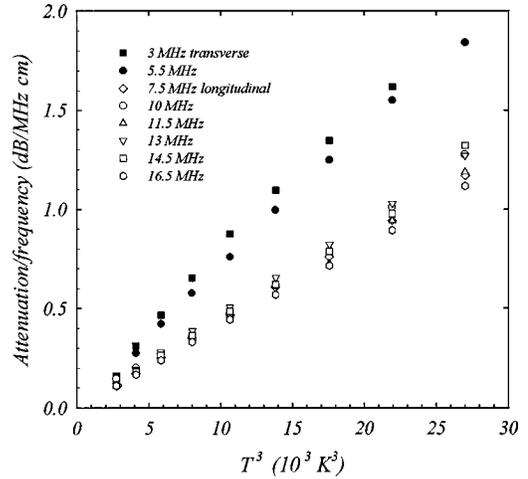


FIG. 4. Damping of longitudinal (open symbols) and transverse (solid symbols) sound in the 360 kg/m³ aerogel showing the frequency independent T^3 damping at low temperatures.

feedthrough from the transducers and amplifier. With our system and samples, this interference was noticeable when the attenuation exceeded about 250 dB/cm and the signal became very small. The variation of the sound velocity with temperature is about twice as large in the low density sample; the change associated with the attenuation peak is about 16%. Although the large attenuation limited the accessible frequency range even more than in the first sample, the attenuation again was proportional to frequency. The behavior of transverse waves was similar; the velocity changes were nearly the same while the attenuation peak occurred at slightly lower temperature than the longitudinal peak. The

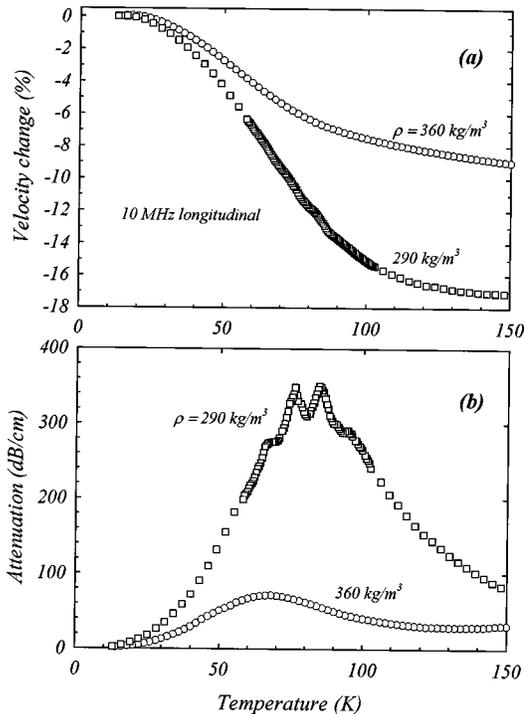


FIG. 5. (a) Comparison of the temperature dependence of the 10 MHz longitudinal sound speeds in aerogels with densities of 360 kg/m³. (b) Attenuation peaks corresponding to the velocity data of (a).

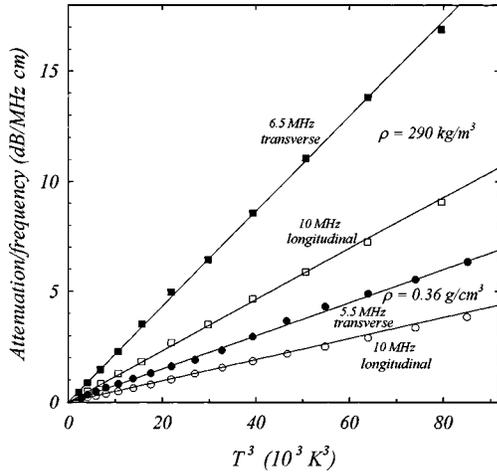


FIG. 6. Low-temperature damping of longitudinal (open symbols) and transverse (solid symbols) sound in 360 kg/m³ (circles) and 290 kg/m³ (squares) aerogels showing T^3 behavior.

low-temperature attenuation for all modes was accurately proportional to T^3 . Figure 6 compares this behavior below 45 K in the two samples. The ratio between the T^3 attenuation in the 290 and 360 kg/m³ samples is about 2.4, whereas the ratio of the attenuations at the peaks is larger, about 5.

DISCUSSION

Below 150 K, we observe attenuation peaks and increases in the speed of ultrasonic waves that are much larger than those in conventional solids but qualitatively resemble those seen in bulk glasses. In bulk silica, the maximum attenuation (for 10 MHz longitudinal sound) occurs around 50 K but is only 1 dB/cm. The corresponding velocity decrease in silica from 10 to 100 K is about 1%; at higher temperatures the sound speeds increase. This behavior of glasses below 100 K is attributed to a thermally activated relaxation process which has its origin in the structural disorder of the glass.

For a relaxation process with a single relaxation time τ , the velocity and attenuation of a sound wave with angular frequency ω are

$$\left(\frac{v_0}{v}\right)^2 = 1 - \frac{v_\infty^2 - v_0^2}{v_\infty^2} \frac{(\omega\tau)^2}{1 + (\omega\tau)^2}, \quad (1)$$

and

$$\alpha = \frac{v_\infty^2 - v_0^2}{2v_\infty^2 v} \frac{\omega^2 \tau}{1 + (\omega\tau)^2}, \quad (2)$$

where v_∞ and v_0 are the velocities in the high ($\omega\tau \gg 1$) and low ($\omega\tau \ll 1$) frequency regimes (which correspond to low and high temperatures, respectively, for a thermally activated process).

The general behavior of the ultrasonic velocity and attenuation in aerogels is consistent with such a relaxation process. Even in aerogels, the total velocity change $\Delta v = v_\infty - v_0$ (a measure of the relaxation strength) is a small fraction of the velocity (i.e., $\Delta v/v \ll 1$). The attenuation peak, which corresponds to $\omega\tau = 1$, then occurs at the temperature where

half the total relaxation velocity change has occurred (and where the slope of the velocity is largest) and the damping at the peak should be

$$\frac{\alpha_p}{\omega} = \frac{1}{2v} \left(\frac{\Delta v}{v} \right). \quad (3)$$

Our ultrasonic measurements on aerogels are generally consistent with a relaxation process with $\tau = 10^{-8}$ s at about 65 K. For a thermally activated relaxation process ($\tau \propto e^{E/kT}$), the attenuation peaks (which occur at $\omega\tau = 1$) shift to higher temperature as the sound frequency increases. In bulk glasses, the frequency dependence of the peak temperature gives² activation energies $E \approx 600$ K. Unfortunately, in aerogels the experimental frequency range is too narrow to determine an activation energy. However, our data have other characteristics of a relaxation process. Figures 2, 3, and 5 show that the peaks occur roughly at the temperatures where the velocity is changing most rapidly (which are slightly lower for transverse waves). Figure 3 confirms the expected frequency independence of the damping (attenuation proportional to frequency). However, Eq. (3) predicts damping peaks of about 36 and 170 dB MHz cm for 10 MHz longitudinal waves in the 290 and 360 kg/m³ aerogels while the actual peaks are smaller, about 7 and 35 dB/MHz cm, respectively. The ratios between the predicted (single τ) and observed attenuation maxima are essentially the same in our two aerogels, about 5. Similar discrepancies are seen in bulk glasses where they have been shown² to result from a distribution of relaxation times τ . The effect of such a distribution is to broaden the attenuation peak and the temperature range over which the velocity change occurs. The total velocity increase Δv is unchanged, but the broadening reduces the height of the attenuation peak. We can also compare the attenuation peaks for longitudinal and transverse modes. Assuming that the same relaxation process affects transverse waves, we would expect (because of the smaller sound speed v) damping peaks that are about 1.7 times larger for transverse waves. From Fig. 3 the actual ratio in the 360 kg/m³ aerogels is about 1.6, in good agreement with Eq. (3).

We conclude that the main features of the ultrasonic behavior of aerogels below 150 K are due to a relaxation process, similar to that in bulk glasses, and that the much larger attenuation peaks and velocity changes in aerogels are consequences of their very small sound velocities. The smaller velocity changes at higher temperatures (see Fig. 1) may be related to the linear increase with temperature seen in tetrahedrally coordinated bulk glasses above the attenuation peak.

The origin of the striking T^3 dependence of the attenuation below about 40 K is less clear. It is not simply the low-temperature tail of the relaxation peak since for $\omega\tau \gg 1$ the attenuation becomes

$$\alpha \approx \frac{1}{v} \left(\frac{\Delta v}{v} \right) \frac{1}{\tau}, \quad (4)$$

which is independent of frequency, in contrast to the observed linear frequency dependence. Also, a process with a thermally activated relaxation time τ would give a low-temperature attenuation that varies exponentially with temperature. In bulk glasses it is not possible to study the low-

temperature ($\omega\tau \gg 1$) behavior of the 50 K relaxation peak since a second attenuation peak is superimposed at low temperatures. This additional attenuation is due to relaxation of the TLS's and, interestingly, is also proportional to T^3 at low temperatures (a reflection of the density of states of the thermal phonons responsible for the TLS relaxation). However, such a mechanism is not likely to be related to the attenuation we see in aerogels since the TLS T^3 attenuation is independent of frequency (in contrast to the attenuation proportional to frequency seen in Figs. 4 and 6). Also, the TLS attenuation in bulk glasses varies as T^3 only at very low temperatures (below about 0.5 K in silica).

One interesting possibility is that the unusual ultrasonic behavior of aerogels is related to their unique fractal structure. This is expected to result in a crossover to localized vibrational modes (fractons) at wavelengths comparable to the aerogel's correlation length and a number of aerogel heat capacity and thermal conductivity measurements^{3,4} have been discussed in terms of fractons. The phonon-fracton vi-

brational spectrum in aerogels has been studied more directly in Brillouin, Raman, and neutron scattering measurements.¹¹ However, in relatively dense aerogels such as ours, the crossover between phonon and fracton behavior occurs at around 10^{10} Hz, far above our ultrasonic frequencies. Although our ultrasonic measurements do not directly probe the fractal structure of aerogels, it is possible that the unusual vibrational density of states affects the relaxation process in aerogels and the resulting sound attenuation and velocity changes. Measurements over a much wider frequency range might shed light on the origin of this ultrasonic behavior in aerogels.

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