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Low-frequency vibrational states in Spectrosil-B

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Abstract. The heat capacity of Spectrosil-B (vitreous silica containing 1200 ppm of OH) has been measured in the temperature range from 2 to 20 K. The heat capacity is closely similar to that of Spectrosil-WF (vitreous silica containing less than 20 ppm of OH). Therefore the heat capacities in the temperature range explored in this work do not depend upon OH concentration. The low-frequency density of vibrational states, $g(\nu)$, has been determined. It has been found that the form of $g(\nu)$ is non-quadratic which can be explained on the basis of the rotational motion of SiO_4 rigid tetrahedra. The Raman and infrared coupling constants have been determined and these are similar. It is found that the form of the Raman coupling constant cannot be explained on the basis of Martin–Brenig theory.

1. Introduction

SiO_2 , commonly known as silica, exists in amorphous and crystalline forms. The two crystalline forms of SiO_2 are quartz and cristobalite. In the vitreous state SiO_2 exists in a variety of forms and is commercially available under a large number of different names such as Amersil, Spectrosil, Heralux, etc. The heat capacities C of various forms of vitreous silica have been measured between 2 and 20 K (Flubacher *et al* 1959, Buchenau *et al* 1986, Ahmad and Hutt 1991). Biliar and Phillips (1975) have measured the heat capacity of cristobalite. There is a great similarity in the plots of C/T^3 as functions of temperature T for vitreous silica and cristobalite. For ready reference the heat capacities of Spectrosil-WF and cristobalite are shown in figure 1. There is a broad peak in the C/T^3 plot at 13.5 K for cristobalite whereas the peak in the C/T^3 plot for vitreous silica is between 9.5 and 10.0 K. C/T^3 values at the peak for vitreous silica and cristobalite are roughly equal and are about seven times higher than the Debye predicted value. This low-temperature behaviour of C clearly shows an enhanced density of states as compared to the Debye density of states, $g_D(\nu)$, which is proportional to ν^2 .

The similarity in the C/T^3 values of vitreous silica and cristobalite has led to a great controversy. For example, Biliar and Phillips (1975) have explained the peak in the C/T^3 plot of cristobalite on the basis of a flat transverse acoustic mode in the perfect cristobalite structure while according to Phillips (1981, 1982) the peak is not intrinsic to the perfect crystal structure but results from transverse acoustic waves at the surface of microtwin boundaries. For vitreous silica, it has been argued (Phillips 1981, 1982, Alexander and Orbach 1982) that the enhanced $g(\nu)$ as compared to

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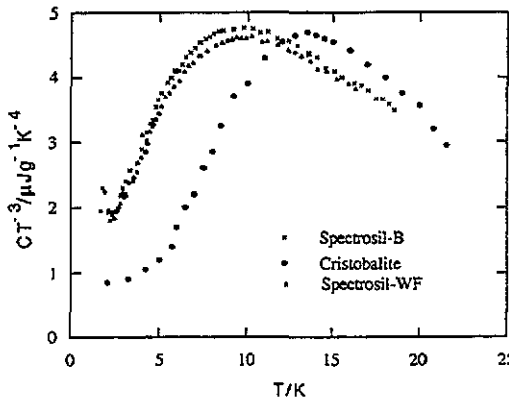


Figure 1. The heat capacities of Spectrosil-B and Spectrosil-WF (present work) and Cristobalite (Biliar *et al* 1975).

$g_D(\nu)$ is due to cross-over from sound waves at low frequencies to vibrations of crystallites or fractals. The fractals of size 5–10 nm, have been assumed to predict this enhancement in $g(\nu)$ in vitreous silica. The clusters proposed by Phillips (1981, 1982) are 6.6 nm sized β -cristobalite crystallites, the surfaces of which are non-coalescing and saturated with Si–O bonds. This assumption of the size of the crystallites is totally incompatible with neutron diffraction and Raman spectroscopic data and has been a subject of widespread criticism (Wright 1985, Galeener and Wright 1986, Buchenau *et al* 1986). In an attempt to identify the nature of the low-frequency vibrational states, we have measured the heat capacity of Spectrosil-B in the temperature range from 1.5 to 18 K and the results are presented in this paper.

2. Measurement of heat capacity

The heat capacity of a small sample (137.4 mg) of Spectrosil-B was measured using a standard heat pulse technique over the temperature range 1.5 to 18 K. A flat surface was ground on the silica sample which was then attached to a silicon-on-sapphire bolometer (Early *et al* 1981) using silicone oil. The results are shown in figure 1. Values of C , believed to be accurate to 3%, are in close agreement with measurements of Spectrosil-WF (Ahmad 1991) but are 20% higher than those of Amersil (Flubacher *et al* 1959) and Heralux (Buchenau *et al* 1986).

3. Results and discussions

The heat capacities of Spectrosil-B and Spectrosil-WF within the experimental accuracy of the system are closely similar. Raman measurements at room temperature (Ahmad 1986) and infrared measurements at 77 K (Hutt 1986) in Spectrosil-B and Spectrosil-WF are also similar and therefore also support these heat capacity results.

The heat capacity results have been fitted, using procedures explained elsewhere (Ahmad 1991), to determine the $g(\nu)$ values at low frequencies ($\nu < 3$ THz). The estimated values of $g(\nu)$ normalized to $g_D(\nu)$ are shown in figure 2. The form of these $g(\nu)$ values is obviously non-quadratic. For $\nu < 0.9$ THz, the form of $g(\nu)$ is $A\nu^2 + B\nu^4$, where A and B are constants. This result is in agreement with theoretical work using the coherent potential approximation by Galperin *et al* (1989).

It may be noted that the heat capacity of cristobalite can be fitted using $g(\nu) \propto \nu^2$ up to 1.09 THz followed by a delta function of width 0.91 THz and magnitude 20 times the Debye value at 1.09 THz. The resulting values of $g(\nu)$ are similar to those determined from lattice dynamics (Ahmad *et al* 1988). In fact, a careful examination of figure 1 reveals that the trends of the heat capacities of cristobalite and vitreous silica are different at low temperatures. The heat capacity of cristobalite after passing through a maxima at 13.5 K decreases and approaches the Debye predicting value whereas in vitreous silica the heat capacity values at low temperature once again show an increase which can be explained on the basis of the two-state tunnelling model.

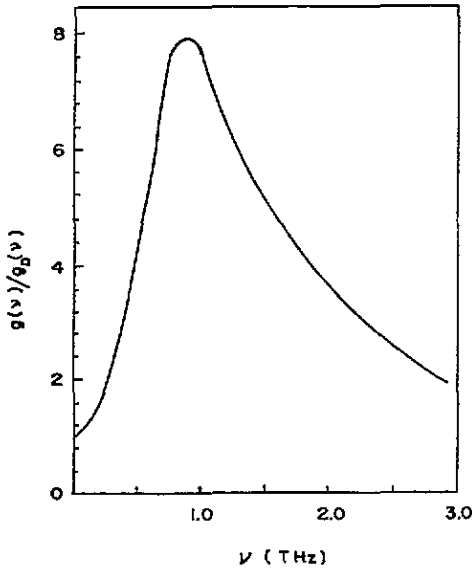


Figure 2. The density of low-frequency vibrational states normalized to the Debye density of states for Spectrosil-B.

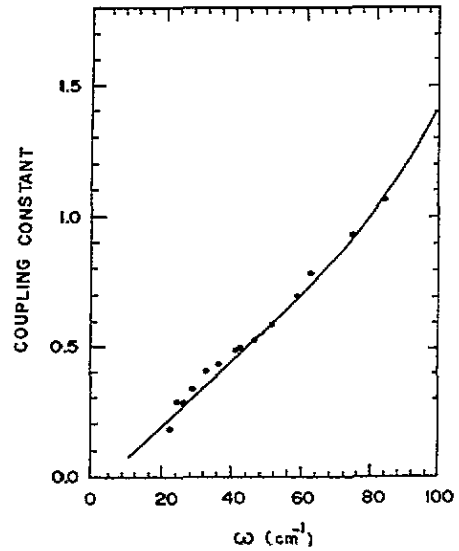


Figure 3. The Raman (solid line) and infrared (dots) coupling constants for Spectrosil-B using $g(\nu)$ determined from heat capacities as shown in figure 2.

It may be noted that $g(\nu)$ values obtained in this work are very reliable as it has been seen in the past (Buchenau *et al* 1986) that the $g(\nu)$ values obtained from heat capacities are identical to those obtained from inelastic scattering of neutrons. Other techniques for the determination of $g(\nu)$ such as Raman scattering and infrared absorption do not provide $g(\nu)$ but a product of $g(\nu)$ and a coupling constant. Using the values of $g(\nu)$ shown in figure 2, the Raman scattering and infrared absorption coupling constants for Spectrosil-B have been determined and are shown in figure 3. It may be seen from this figure that they are similar. The conclusion to be drawn from this comparison is that in Spectrosil-B, there is no need to introduce separate charge and structural correlation lengths for infrared and Raman experiments. In both cases a vibrational correlation function $C(\nu)$ is the important physical parameter. The theoretical work also predicts this similarity (Ahmad and Hutt 1991). A similar vibrational function has been used by Jäckle and Fröbose (1979) when calculating the neutron elastic structure factor in glasses, and this suggests that a complete synthesis of neutron, infrared and Raman measurements, based on this idea, should be possible in this low-frequency range.

The Martin–Brenig theory (Martin and Brenig 1974) as normally applied assumes that the Raman coupling constant $C(\nu)$ is

$$C(\nu) \propto \nu^2 \exp \left[-(2\pi\nu\sigma/v_s)^2 \right] \quad (1)$$

where v_s is the velocity of sound and σ is the structural correlation range. It is clear from figure 3 that the Raman coupling constant cannot be represented by equation (1). Therefore the Martin–Brenig model as normally applied is not valid if the $g(\nu)$ values determined from heat capacities are used. The experimental work by Malinovsky *et al* (1990) also confirms the present conclusions regarding the Martin–Brenig approach. It is easy to see what is going wrong. Martin and Brenig calculate the contribution of a plane wave of wave vector q , and this is usually taken to represent the Raman scattering in the glass of angular frequency $\omega = v_s q$. This is consistent with the normal assumption $g(\nu) \propto \nu^2$, but both these approximations are valid only at very low frequencies. In a real glass higher-frequency vibrational modes ($\nu > 0.3$ THz) are either strongly attenuated plane waves or ‘localized’ vibrations. The word ‘localized’ is used here not to imply lack of thermal transport, but to indicate that a vibrational mode will involve a large range of wave vectors q if analysed into plane waves. When using the Martin–Brenig model, the contribution at angular frequency ω should be calculated by summing over the appropriate q -vectors, most conveniently accomplished by means of a spectral function. This does not appear to have been done, but will clearly lead to a constant $C(\nu)$ at higher frequencies where a broad range of q is expected.

The approach that the peak in C/T^3 values of cristobalite is not intrinsic to the perfect crystal structure but results from transverse acoustic waves at the surface of microtwin boundaries (Phillips 1985, 1987a) has been criticized on the basis that it involves a misappreciation of the transverse acoustic (TA) model and an incomplete assessment of the available experimental data on the subject (Phillips 1987b). In our previous work (Ahmad *et al* 1988), it has been shown that a satisfactory description of the lattice dynamics of cristobalite is possible using only three force constants, i.e. bond stretching and bond bending at both silicon and oxygen atoms. The calculated density of vibrational states by direct sampling gives a low-temperature heat capacity in reasonably good agreement with experimental data. These calculations strongly support the picture that the peak in the low-temperature heat capacity of cristobalite results from a non-dispersive TA branch and not from the imperfections in the crystal structure as claimed by Phillips (1985, 1987a).

A possible explanation for the enhanced $g(\nu)$ as compared to $g_D(\nu)$ in vitreous silica is the cross-over from sound waves at low frequencies to vibrations of crystallites or fractals (Phillips 1981, 1982, Alexander and Orbach 1982). Fractals of size 5–10 nm have been assumed to predict this enhancement in $g(\nu)$. The clusters proposed by Phillips (1981, 1982) comprise 6.6 nm size β -cristobalite crystallites, the surface of which are non-coalescing and saturated with Si–O double bonds. This assumption of the size of the crystallites is totally incompatible with the neutron diffraction studies as the width of the diffraction pattern indicates a correlation length of no more than 1 nm (Wright 1985). Assuming the presence of 1 nm size β -cristobalite crystallites in vitreous silica, the model calculations by Wright (1985) for the neutron diffraction pattern give rise to three peaks below 0.53 nm^{-1} whereas experimentally only two peaks are observed. Since this region of the diffraction pattern is most sensitive to intermediate-range order, the presence of fractals or β -cristobalite crystallites of

size 5–10 nm is out of the question. Further evidence against the presence of β -cristobalite crystallites in vitreous silica comes from the study of the devitrification process in pure bulk vitreous silica. This process has been observed to start from the surface of the sample and to proceed inwards (Sosman 1965 in Galeener *et al* 1983), which is contrary to what would be anticipated for a material with paracrystallites. It is therefore concluded that the experimental evidence does not support the fractal model.

A more convincing and concrete explanation about the nature of these additional states has been given by Buchenau *et al* (1986) based on inelastic neutron scattering studies, heat capacity measurements and model calculations. It was shown that in vitreous silica (Heralux) the additional states can result from relative rotational motion of almost rigid SiO_4 tetrahedra. Model calculations also support this picture (Guttman *et al* 1986). They also show that the frequencies would approach zero in a structure based on linked tetrahedra so that the structure would become locally unstable, giving rise to two-level potentials consistent with what are known as tunnelling states at low temperatures. Thus the model based on microscopic motion of rigid tetrahedra provides an explanation both for the heat capacity and the presence of double-well potentials.

4. Conclusions

The estimated form of density of low-frequency vibrational states ($\nu < 2.5$ THz) in Spectrosil-B is non-quadratic. The additional modes as compared to the Debye density of states can be attributed to rotational motion of almost rigid SiO_4 tetrahedra. Such degrees of freedom also provide a possible explanation for the presence of two-well tunnelling states. The forms of the Raman and infrared coupling constants are similar. The Raman coupling constant cannot be represented according to Martin-Brenig theory if the $g(\nu)$ values determined from heat capacities are used.

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